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Doctor's Dissertation

The Demonstration of Electron-Transfer Reactions and Their Effect on Model Lignin Condensation Reactions Under Alkaline Pulping Conditions

Dean A. Smith

June, 1986

THE DEMONSTRATION OF ELECTRON-TRANSFER REACTIONS AND THEIR EFFECT ON MODEL LIGNIN CONDENSATION REACTIONS UNDER ALKALINE PULPING CONDITIONS

A thesis submitted by

Dean A. Smith

B.S. 1980, The Ohio State University

M.S. 1982, Lawrence University

in partial fulfillment of the requirements
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Appleton, Wisconsin

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THESIS SUMMARY

The alkaline reactions of two lignin model compounds, 3,5-dimethoxy-4-hydroxybenzyl alcohol (syringyl alcohol) and 5,5-dimethyl-6-hydroxy-6-(3,5-dimethoxy-4-hydroxyphenyl)-1-hexene, were studied in order to demonstrate the possible existence of radical lignin reactions during the alkaline pulping of wood. When syringyl alcohol was reacted in 1N NaOH at 135°C, three monomers and two dimers were produced. Two of the products were presumably formed by radical intermediates. For various reasons, the addition of radical initiators and inhibitors to the alkaline reaction of syringyl alcohol gave inconclusive results about the extent of radical reactions with this model.

Typical pulping reagents (anthrahydroquinone, glucose, and NaSH) were also added to the alkaline reaction of syringyl alcohol. Anthrahydroquinone and glucose increased the yields of the radical derived products, presumably by transferring electrons to quinonemethides (QMs), which are formed when syringyl alcohol is heated in alkali. Hydrosulfide, however, depressed the formation of the radical products; hydrosulfide apparently interacts by an ionic pathway.

The phenolic hexene compound mentioned above was heated in 1N NaOH at 135°C to afford a small yield of 1,1,3-trimethyl-2-(3,5-dimethoxy-4-hydroxyphenyl)-cyclopentane. The cyclization of a hexenyl group to a five-membered ring is diagnostic of a radical intermediate. Apparently, phenolate ions are capable of transferring electrons to QMs. The addition of either anthrahydroquinone or glucose to the alkaline reaction of the hexene compound greatly enhanced the production of the cyclized product; hydrosulfide, however, did not. The addition of glucose also gave three additional cyclized products, 4-methoxy-, 6-methoxy-, and 4,6-dimethoxy-12,12-dimethyl-5-hydroxy-tricyclo [7.3.0.$0^{2,7}$] 2,4,6-dodecatriene. The production of the cyclized products in the glucose reaction indicates that the radical intermediates are longer lived in this case.

The ability of anthrahydroquinone and glucose to transfer electrons to QMs in aqueous alkali has implications as to how they affect the rate of lignin fragmentation and condensation reactions during the alkaline pulping of wood. The results of the two models indicate that anthrahydroquinone and glucose are able to prevent condensation reactions by reducing potential QM precursors to structures which are no longer able to directly form a QM. Hydrosulfide, on the other hand, appears to inhibit condensation reactions by reversibly adding to (and thereby lowering the concentration of) intermediate QMs.

THESIS INTRODUCTION

Wood is basically composed of two polymers, carbohydrates and lignin. Lignin is a very complex polymer (Fig. 1) containing phenylpropane units linked by a variety of bonds, most of which are carbon-oxygen linkages. The remaining bonds are strong carbon-carbon linkages. The goal of the alkaline pulping processes of wood is to remove the lignin and retain the carbohydrates.

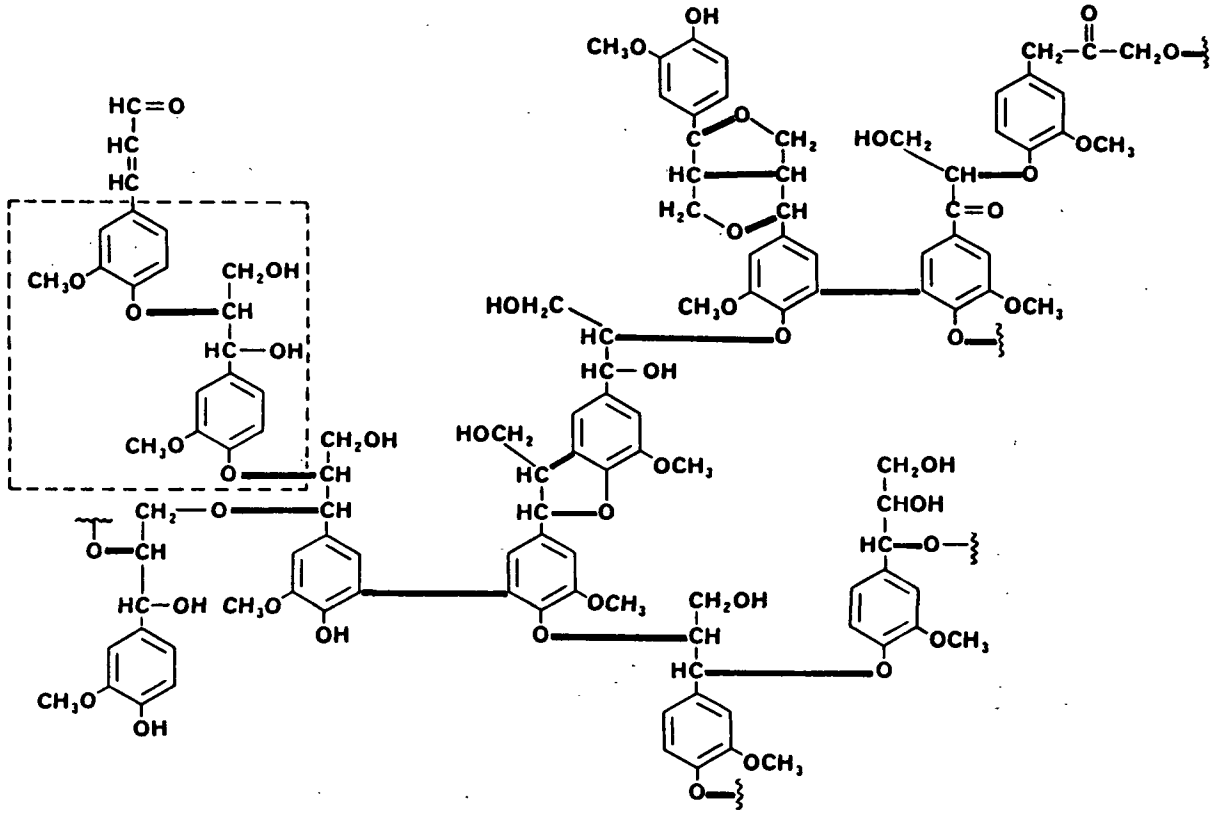


Figure 1. A literature representation[1] of a softwood lignin polymer. The bold lines indicate linkages between phenylpropane units while the dotted square outlines the most common linkage in lignin, a β-aryl ether.

The majority of the alkaline reactions of lignin can be classified as either fragmentation or condensation.[2,3] Fragmentation is the desired reaction involving the cleavage of linkages between lignin units; the polymer is broken

down into small water-soluble molecules. Condensation, on the other hand, is an undesired reaction resulting in the lignin being chemically bonded into a larger macromolecule; condensation can be thought of as the reverse of delignification. The condensed lignin contains many of the strong carbon-carbon linkages, which are very difficult to fragment.[3]

Several methods are employed to remove lignin from wood, and one of these is the alkaline kraft process. Kraft delignification occurs in three phases (Fig. 2), the initial, bulk, and residual phases.[4] The initial phase occurs during the heating of the wood to the reaction temperature; the phenolic α-aryl ether linkages are fragmented during this phase. The bulk phase begins about the time the wood reaches the reaction temperature, which is approximately 170°C. During the bulk phase, the carbon-oxygen linkages which require greater energy for cleavage are the majority of the linkages fragmented.

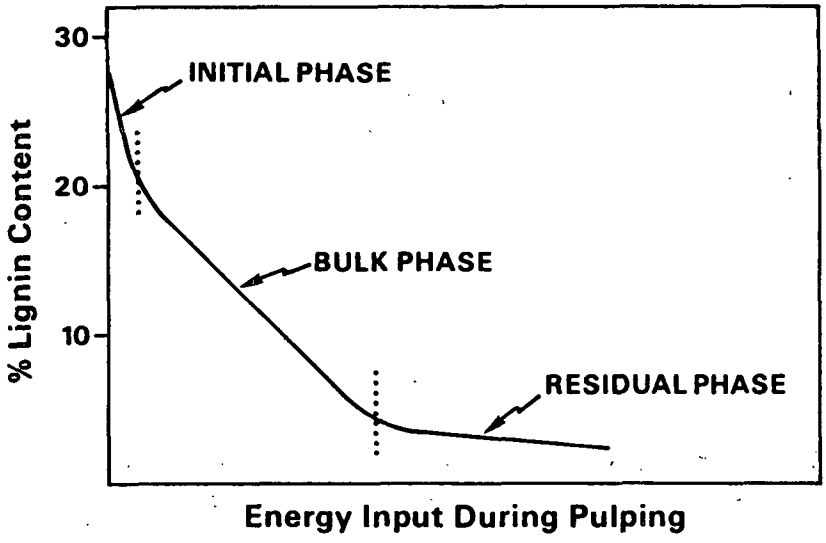


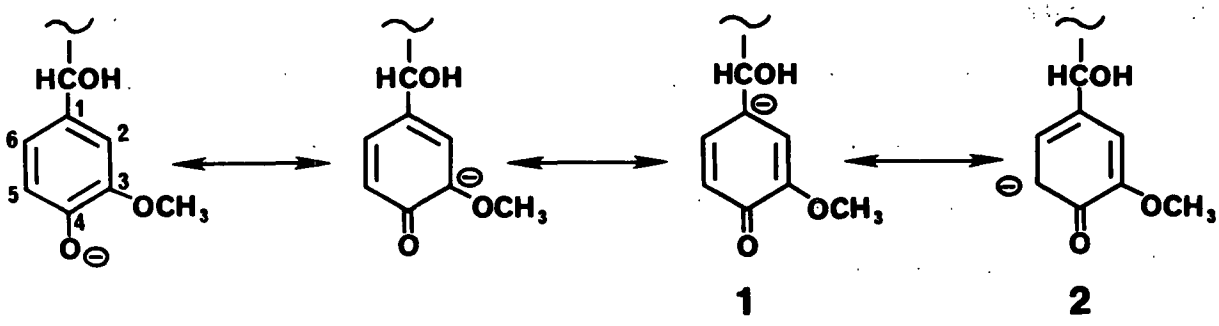
Figure 2. The three phases (initial, bulk, and residual) of the kraft delignification of a softwood.

Finally, the residual phase begins, which is characterized by the need of a great deal of time to remove a small percentage of the remaining lignin. Since

the carbohydrate yield continually decreases as a function of time at 170°C, kraft delignification is normally terminated as near to the end of the bulk phase as possible.[3] The remaining lignin, termed residual lignin, is either left in the pulp or removed by bleaching. This residual lignin contains a higher degree of carbon-carbon linkages as compared to the native lignin. Thus, the condensation reactions which occurred during kraft delignification are considered to be at least partially responsible for residual lignin.[3]

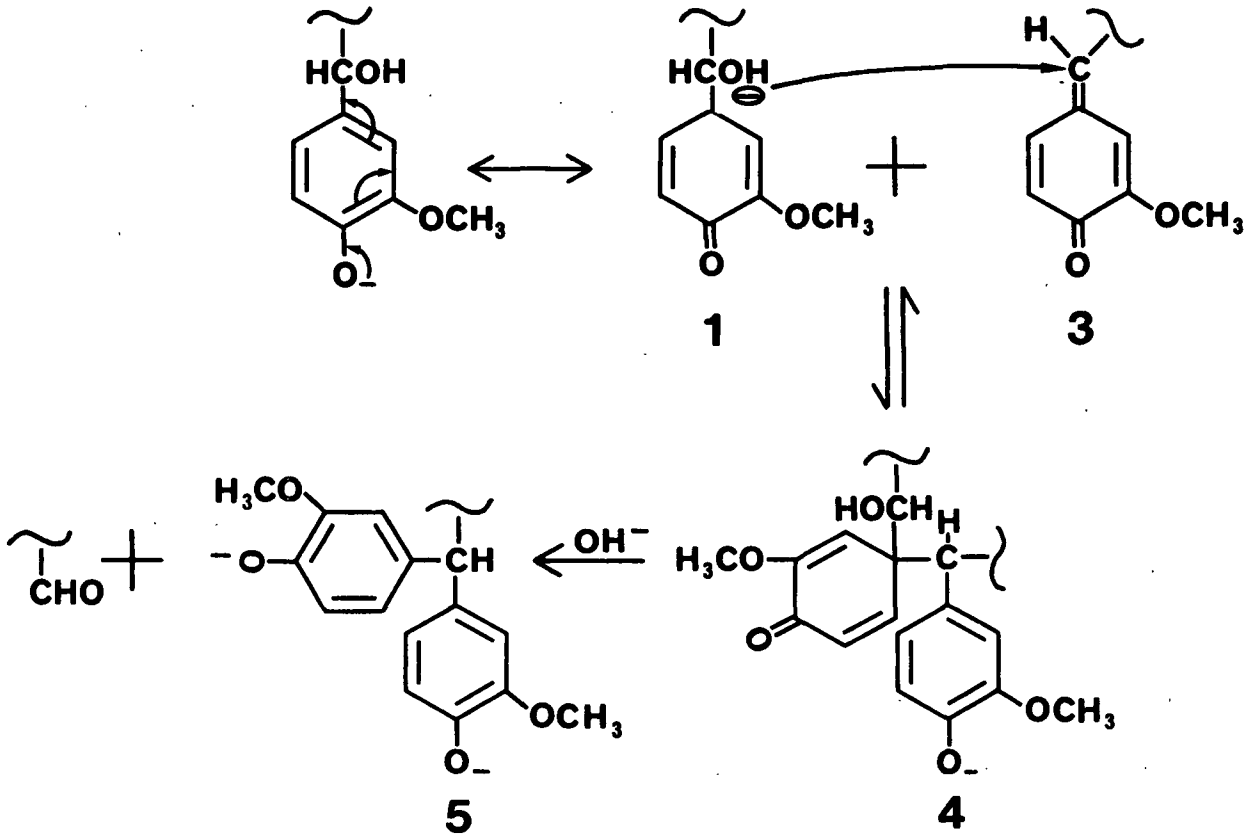
An understanding of condensation reactions may allow methods to be employed to reduce or prevent their occurrence. Retardation of condensation should result in a decrease in the pulping time by a combination of two effects: (a) dissolved lignin would remain in solution and (b) pulping-resistant carbon-carbon bonds would be minimized. Thus, the carbohydrate yield would be increased and, with a reduction in the amount of residual lignin, the bleaching requirement would be decreased.

The mechanism of condensation is believed to be by the conjugate addition of carbanions to quinonemethides (QMs),[5] or in other words, by ionic pathways. Two pathways of condensation, resulting in the formation of α-1 and α-5 products,[6] will be described. Under the conditions employed in alkaline pulping systems, all phenols are ionized. This ionization increases the electron density at three sites of the aromatic ring, namely at C-1, C-3, and C-5 [shown in Eq. (1)]. The increase in electron density at C-1 is represented by resonance structure **1**. Formation of the α-1 product begins with the nucleophilic attack by C-1 of **1** on the α-carbon of a QM (**3**), forming an intermediate (**4**) which contains a new carbon-carbon bond (Scheme 1). Ionization of the hydroxyl group of **4** allows for the elimination of an aldehyde and a rearomatization of the ring, yielding the α-1 condensation product (**5**).



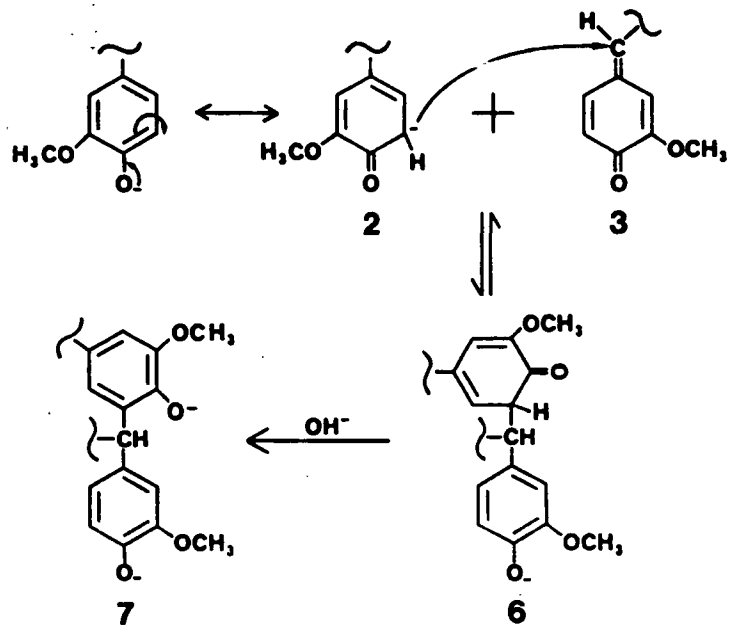
(1)

Scheme 1. The ionic α-1 condensation mechanism.



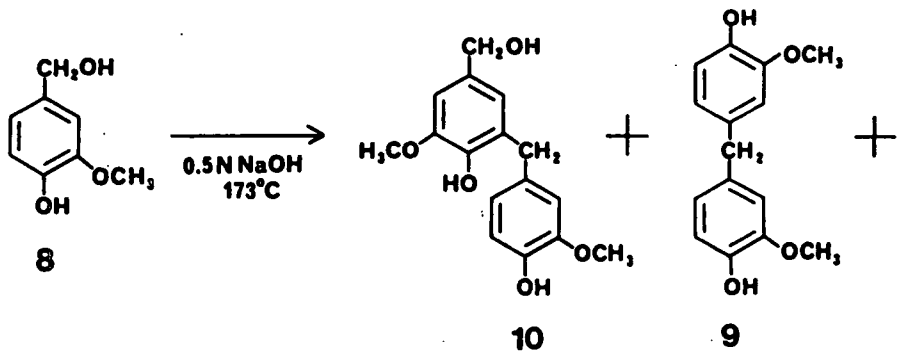
Formation of α-5 condensation products is similar. An ionized phenol increases the electron density at C-5 (2), which allows for the addition of C-5 to the α-carbon of a QM by the formation of a carbon-carbon bond (intermediate **6**), as shown in Scheme 2. Deprotonization by hydroxide rearomatizes the ring to give the α-5 condensation product (7). Once again, two lignin units are linked by a carbon-carbon bond.

Scheme 2. The ionic α-5 condensation mechanism.



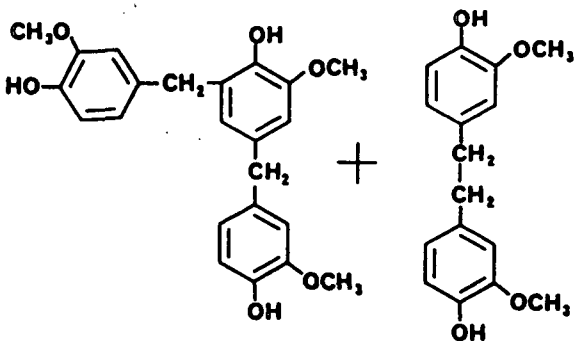
A previous investigation[7] of condensation studied the alkaline reaction of a simple lignin model compound, vanillyl alcohol (**8**). When vanillyl alcohol was reacted in 0.5N NaOH at 173°C, several condensation products were produced [Eq. (2)]; included among the products were the α-1 and α-5 dimers (**9** and **10**, respectively), a trimer comprised of α-1 and α-5 condensation (**11**), and di-1,2-(3-methoxyl-4-hydroxyphenyl)-ethane (biguaiacyl, **12**). Biguaiacyl is a dimer which cannot be formed by the traditional ionic mechanisms of condensation; a radical intermediate was hypothesized as being responsible for the formation of this dimer.

Also included in the vanillyl alcohol study was an investigation of the effect of various additives on the condensation of vanillyl alcohol. The addition of anthrahydroquinone (AHQ) as glucose/anthraquinone was found to dramatically reduce the production of dimers and trimers. Another compound, 3,5-dinitrobenzoic acid, was added as a radical inhibitor and was found to reduce



8 10 9

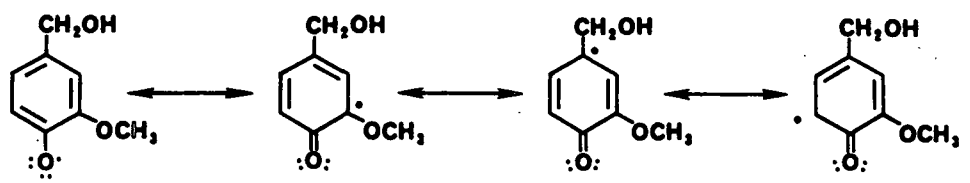
(2)



11 12

condensation. Consequently, the possibility of a radical mechanism of condensation was hypothesized, since AHQ and a radical inhibitor were observed to reduce condensation and a dimer, biguaiacyl, was presumably formed by radical intermediates.

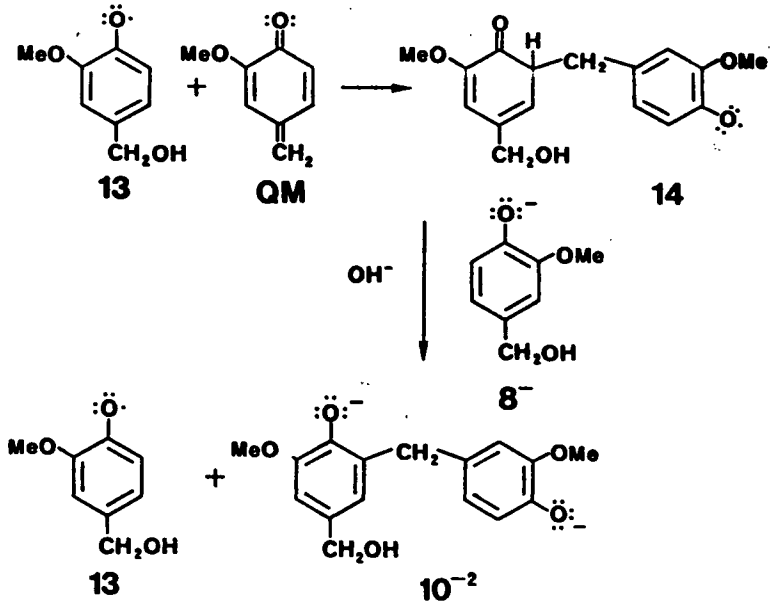
While the proposed ionic mechanisms of condensation are plausible, there exists no experimental proof of their occurrence. Another plausible mechanism of condensation involves phenolate radicals (13) as the reactive species (in place of phenolate ions). Resonance structures place the radical at the same three sites of the aromatic ring as a phenolate ion [Eq. (3)]. This allows for the formation of the observed condensation products; the route for the



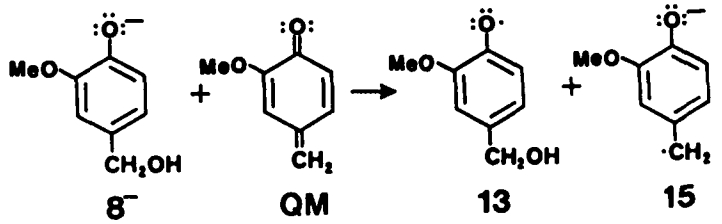
13 (3)

formation of the α-5 product of vanillyl alcohol is shown in Scheme 3. One of the final steps of the radical mechanism is the transfer of an electron from a phenolate ion to radical intermediate **14**, resulting in a fully ionized product and a new phenolate radical. The new phenolate radical could possibly be a new reactive species (such as **13**) which would then be able to undergo further condensation. Thus, a cyclic radical mechanism could be responsible for condensation.

Scheme 3. The radical α-5 condensation mechanism.

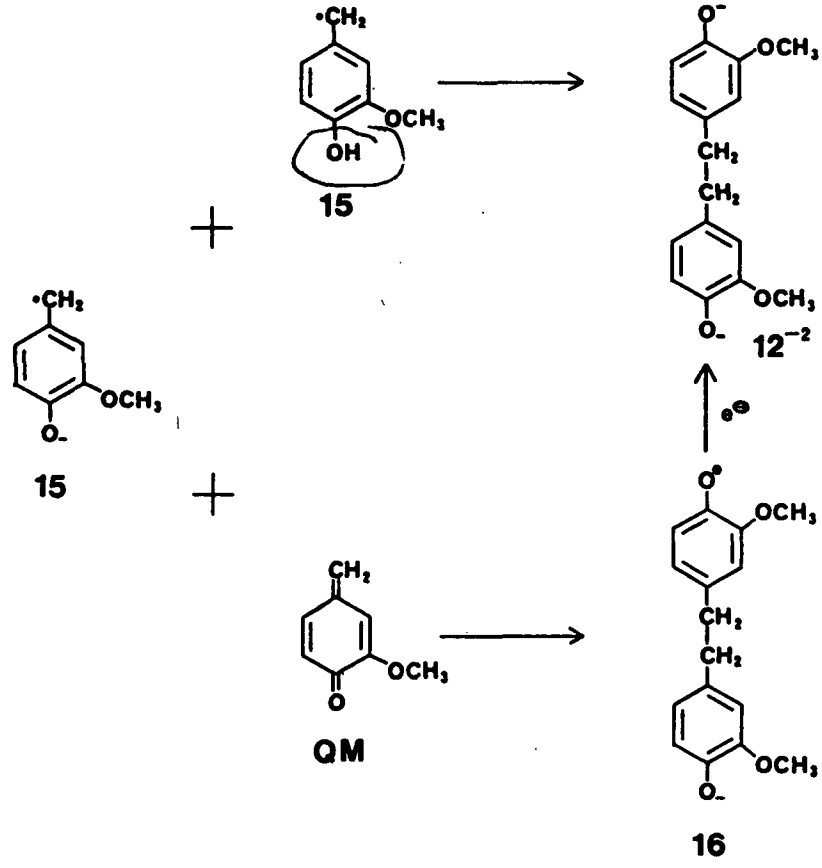


A possible source of phenolate radicals could be from the transfer of an electron from a phenolate ion to a QM [Eq. (4)]. This transfer generates a reactive phenolate radical and a quinonemethide radical-anion ($QM^{\bullet-}$). The $QM^{\bullet-}$ (**15**) could lead to the formation of biguaiacyl by coupling with another $QM^{\bullet-}$ (Scheme 4). Alternatively, the $QM^{\bullet-}$ could also attack the α-carbon of a QM to form a biguaiacyl radical-anion (**16**), which would subsequently acquire an electron to form biguaiacyl. Due to the small amount of $QM^{\bullet-}$s produced, the more likely route of biguaiacyl formation is by the pathway of QM attack.

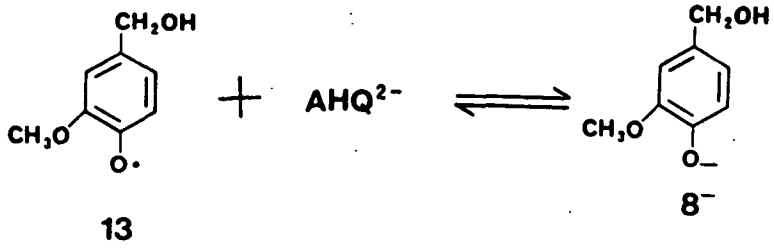


(4)

Scheme 4: Formation of biguaiacyl by a QM$^{\cdot-}$ intermediate.



The observed decrease in condensation with addition of AHQ may be because AHQ^{-2} transfers an electron to a phenolate radical, forming a less reactive phenolate ion and $AHQ^{\cdot-}$ [Eq. (5)]. In this manner, AHQ^{-2} would be quenching radical intermediates and thus be acting as a radical inhibitor of condensation.

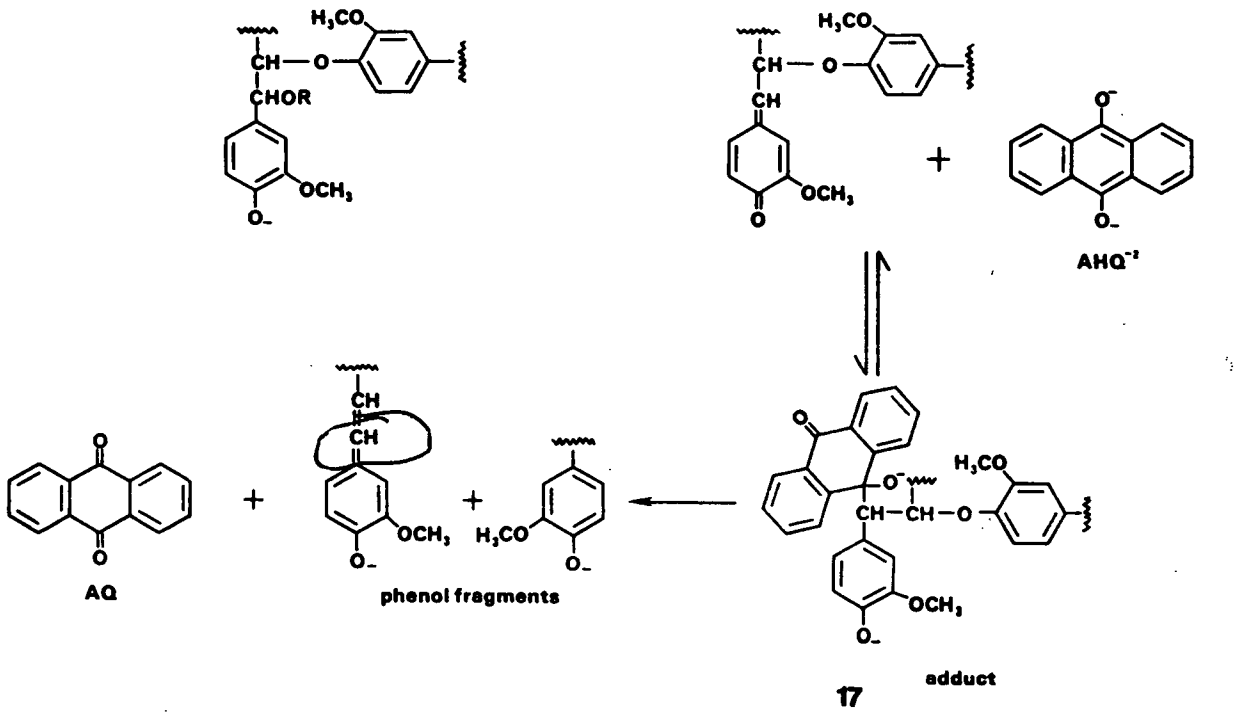


(5)

Besides the possibility of radicals in condensation reactions, evidence has been accumulating that fragmentation may also be by radical intermediates.[9-12] Previously, ionic mechanisms involving adduct intermediates have been proposed for the fragmentation of β-aryl ether bonds by pulping additives.[13-15]

For AHQ promoted fragmentation, the ionic mechanism begins with a carbanion attack by AHQ^{-2} on the α-carbon of a QM to form the adduct (17) as shown in Scheme 5. This step is very similar to the initial steps of α-1 and α-5 condensation. The adduct is believed to break apart with a concerted cleavage of the β-aryl ether bond and the concurrent generation of anthraquinone.

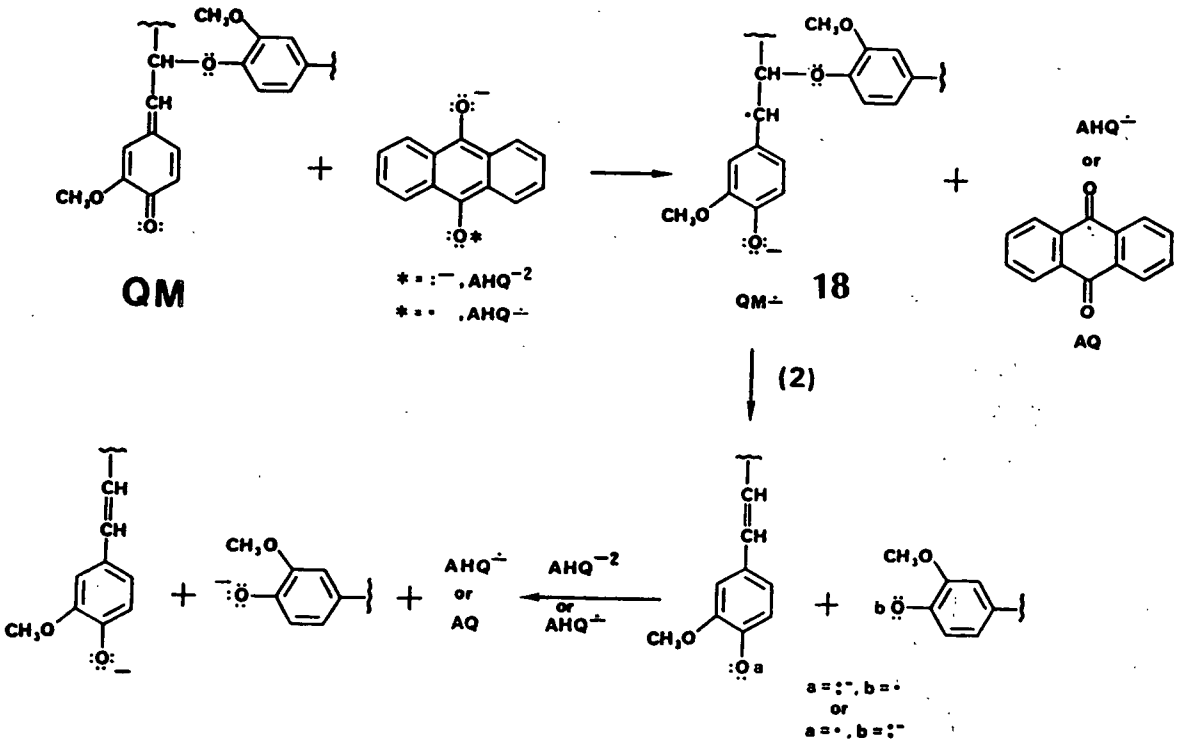
Scheme 5. Delignification by an AHQ adduct - ionic mechanism.



Recent evidence, however, has indicated that AHQ ions can electron-transfer to QMs.[9] This transfer would result in a $QM^{\cdot-}$ (18), which could presumably fragment to a phenolate ion and a phenolate radical (Scheme 6). Evidence supporting an electron-transfer process was provided by a study of the cleavage of

a β-aryl ether QM in solution with electrochemically generated $AHQ^{\cdot-}$.[10] Cleavage of the β-aryl ether bond was postulated to be a result of electron-transfer from $AHQ^{\cdot-}$ to the QM, providing a $QM^{\cdot-}$ which subsequently fragmented. The study, however, employed conditions quite different from pulping; the temperature was ambient and the solvents were principally organic.

Scheme 6. Delignification by AHQ^{-2} electron-transfer to QMs.



Recently, Fullerton, et al., have shown that fragmentation of a β-aryl ether lignin model was promoted by "reducing sugars" and organometallic compounds.[16,17] Ionic mechanisms with adduct intermediates were proposed as the route to fragmentation. Once again, the increase in the fragmentation rate could be due to an electron-transfer mechanism and not an ionic mechanism, just as with AHQ.

In summary, radical reactions may be key steps in both lignin fragmentation and condensation processes during the alkaline pulping of wood. If electron transfer to QMs during pulping leads to the promotion of fragmentation and the retardation of condensation reactions of lignin, then possible future research in pulping catalysts will be to find better electron-transfer reagents. What remains to be proven is that the proposed electron-transfer reactions can occur in aqueous alkali at elevated temperatures and that they are beneficial to efficient pulping.

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THESIS OBJECTIVES

1. To determine the importance of radicals in lignin condensation reactions

2. To determine whether AHQ and other pulping reagents can transfer electrons to QMs under the conditions of pulping (approximately 1N NaOH at high temperatures)

To achieve the objectives of the thesis, we studied the alkaline reactions of two lignin model compounds, syringyl alcohol and a model which we refer to as the "electron-transfer detector" compound. Syringyl alcohol was used to determine the importance of radical intermediates in condensation reactions, while the electron-transfer detector compound was used to detect the transfer of electrons to QMs in 1N NaOH solutions. The results of the study of these two compounds is the subject of the remainder of the thesis and will be presented in article format and appendixes.

SYRINGYL ALCOHOL CONDENSATION REACTIONS - A SEARCH FOR RADICAL REACTIONS

Dean A. Smith and Donald R. Dimmel
The Institute of Paper Chemistry
Appleton, Wisconsin 54912

ABSTRACT

Syringyl alcohol, a simple lignin model compound, has been heated in 1N NaOH at 135°C. Five products (three monomers and two dimers) were identified from the reaction mixture; two of the products were presumably formed by radical processes. One of the radical products, 4-methylsyringol, was shown by deuterium labeling to incorporate a benzylic hydrogen from a syringyl alcohol molecule. Radical initiators and inhibitors, which were added to alkaline reactions of syringyl alcohol in an attempt to determine if condensation proceeded by a radical mechanism, gave inconclusive results.

Typical pulping reagents (anthrahydroquinone, glucose, and sodium sulfide) were also added to the alkaline reaction of syringyl alcohol; the reaction progress was followed over a four-hour period. Anthrahydroquinone and glucose increased the yields of the radical products, presumably by transferring electrons to intermediate syringyl quinonemethides. Sulfide, on the other hand, gave results which were interpreted to involve a reversible ionic interaction between hydrosulfide and syringyl alcohol.

INTRODUCTION

The reactions of lignin during the alkaline pulping of wood are basically of two types, fragmentation and condensation.[1,2] Fragmentation is the desired reaction, involving the breaking down of the lignin polymer into small, water-soluble particles. Condensation, on the other hand, is an undesired reaction resulting in the lignin being chemically bound into a larger molecule. The condensed lignin is believed to contain many strong carbon-carbon linkages between monomers and to be at least partially responsible for residual lignin.[2]

The majority of the investigations into the alkaline reactions of lignin have concentrated on fragmentation mechanisms.[3] As a result, little is known about the importance of condensation during pulping or what methods can be

employed to prevent its occurrence. The generally accepted mechanism of condensation involves the conjugate addition of carbanions to quinonemethides (QMs), or in other words, involves ionic pathways.[3] However, experimental evidence in support of this mechanism is not readily apparent.

One study of condensation,[4] using the lignin model vanillyl alcohol, demonstrated the ability of anthrahydroquinone (AHQ) to reduce the amount of dimers and trimers formed; however, the mechanism was not elucidated. Also, in the vanillyl alcohol study a dimer was isolated whose formation could not be explained by ionic mechanisms; the occurrence of some radical reactions was hypothesized.

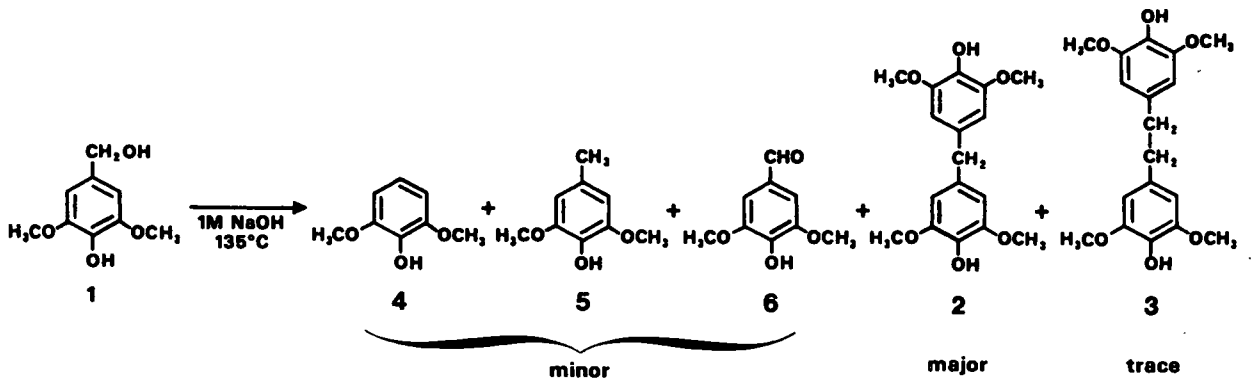
Another condensation study[5] concerned the reactions of coniferyl alcohol with a low molecular weight lignin isolated from a kraft wood pulping liquor. Addition of either sodium sulfide or AHQ to the reaction system reduced the amount of condensation. Once again, the mechanisms by which sulfide and AHQ were able to reduce condensation were not determined.

The condensation reactions of a lignin model compound, syringyl alcohol (1), is the subject of this report. Syringyl alcohol offers the advantage of only one site for condensation; the formation of products larger than dimers is prevented, allowing a simple product analysis. Investigations were conducted of the effects of various additives on the condensation reactions of syringyl alcohol, with emphasis placed on the mechanisms by which typical pulping additives are able to reduce condensation.

RESULTS AND DISCUSSION

SODIUM HYDROXIDE REACTION

Heating syringyl alcohol in 1N NaOH at 135°C produced five products. Disyringylmethane (2), the expected condensation dimer, was the major product. Another dimer, bisyringyl (3), was formed in a trace amount. Three monomers, syringol (4), 4-methylsyringol (5), and syringaldehyde (6), were produced in moderate yields [Eq. (1)]. The concentrations of syringyl alcohol and its products (except bisyringyl) are shown in Fig. 1-5 over a four-hour reaction period.



(1)

Syringol and 4-methylsyringol are products whose analogs, guaiacol and creosol, were not observed in the vanillyl alcohol study.[4] While the formation of syringol cannot be conclusively explained, the mechanism responsible for the formation of 4-methylsyringol, along with bisyringyl, appears to be radical in nature. (Concentration curves will be given for syringol, but since syringol gave results which could not be interpreted to provide any useful information about the alkaline reaction of syringyl alcohol, there will be no further discussion about its formation.)

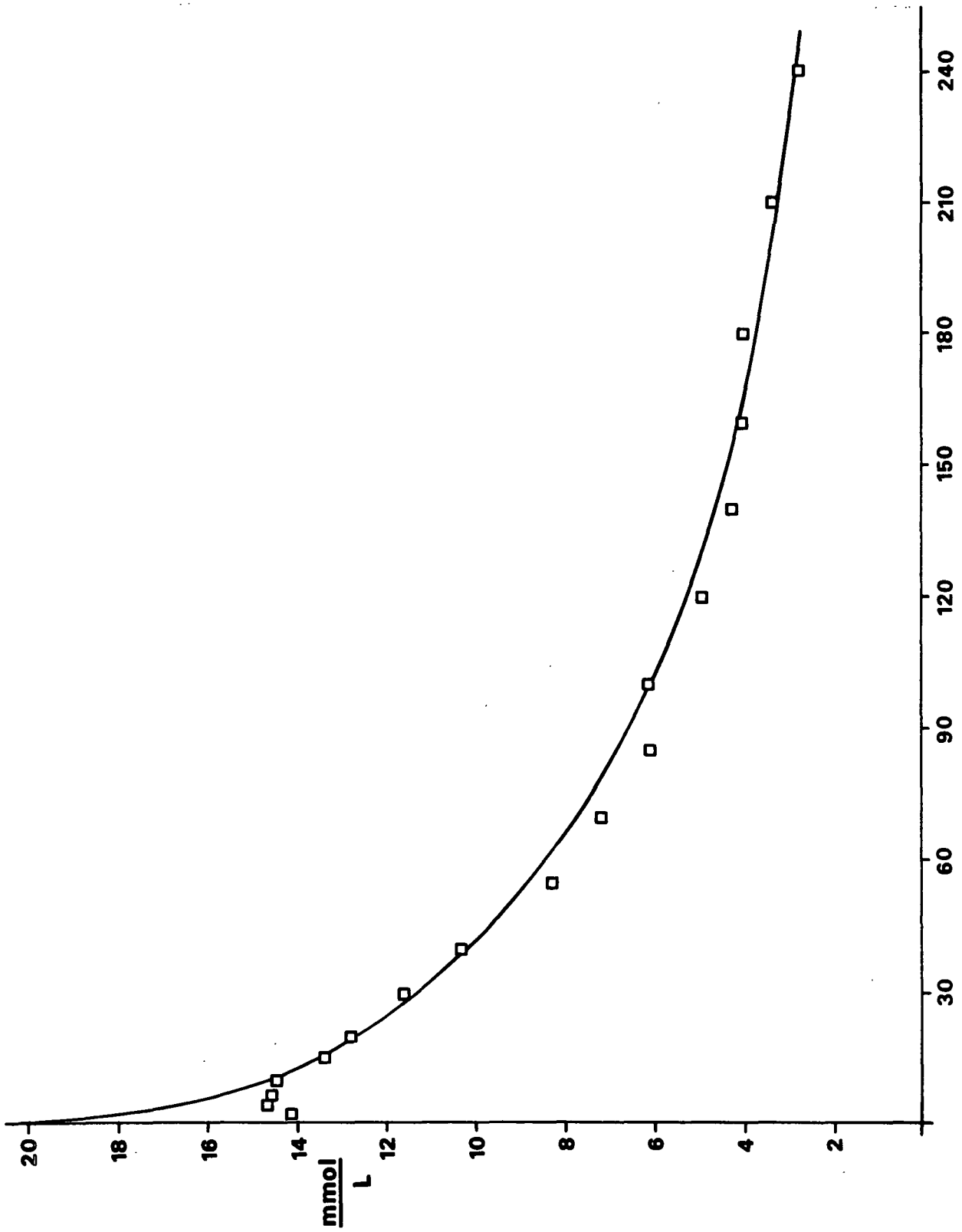
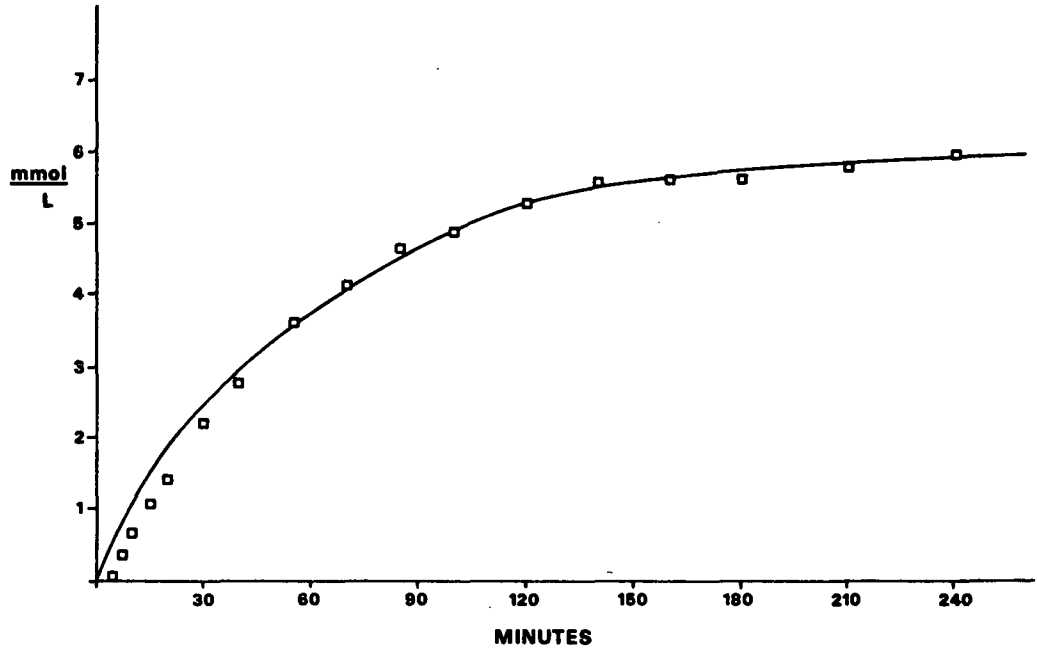
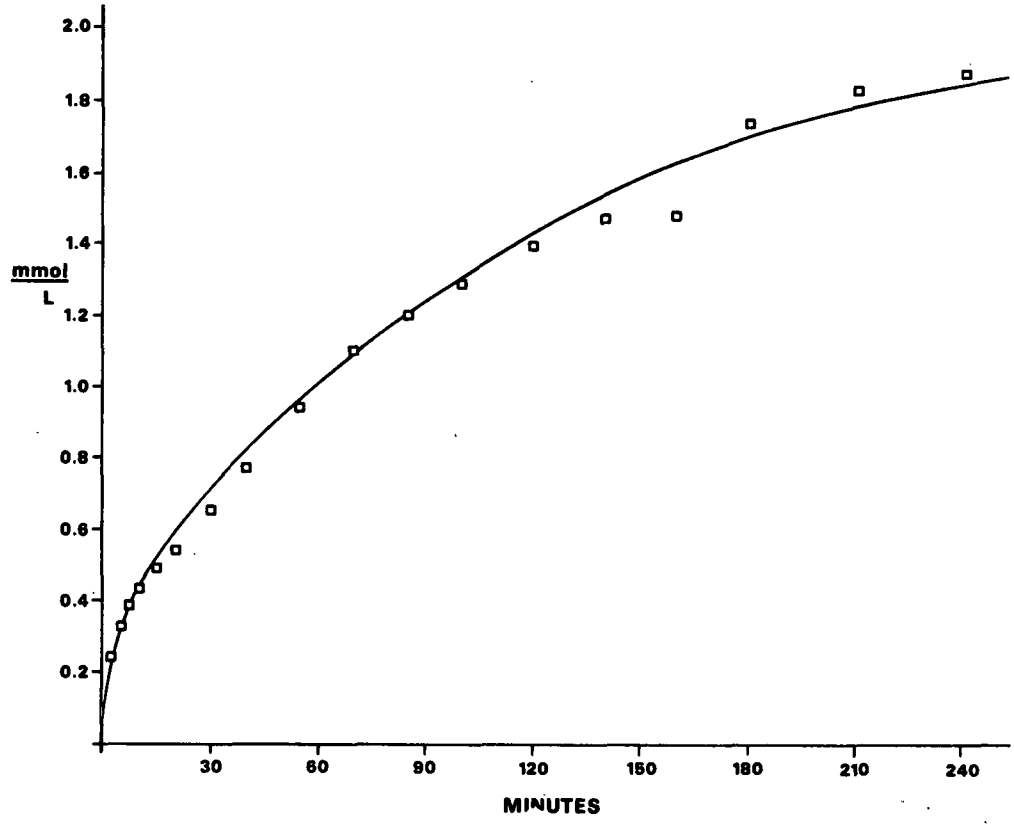
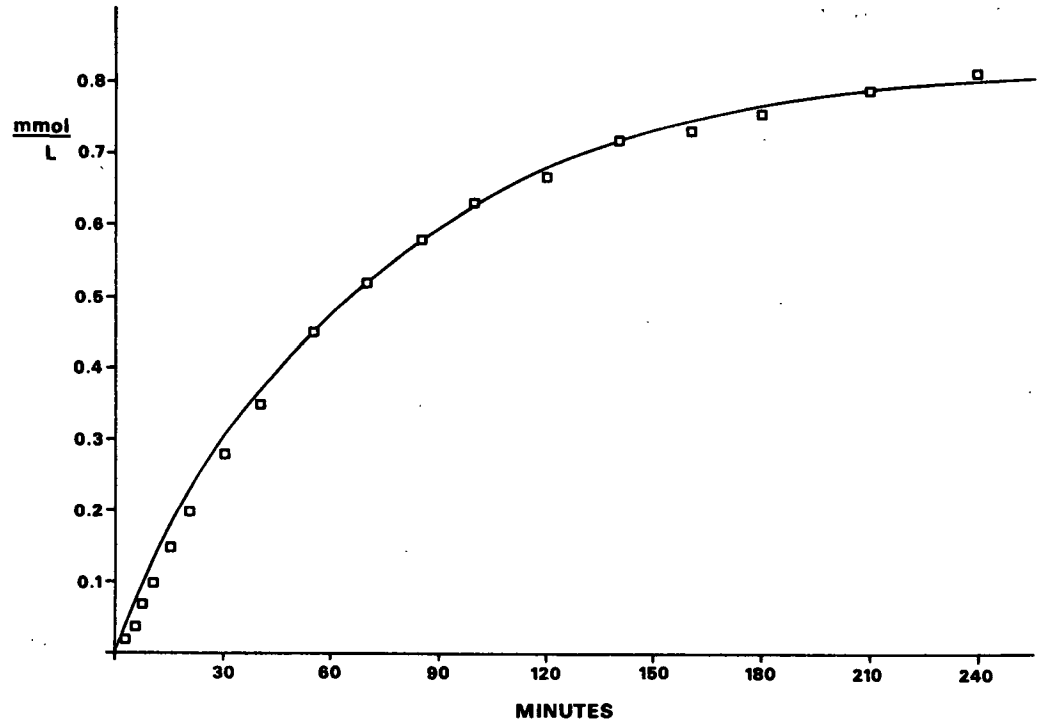


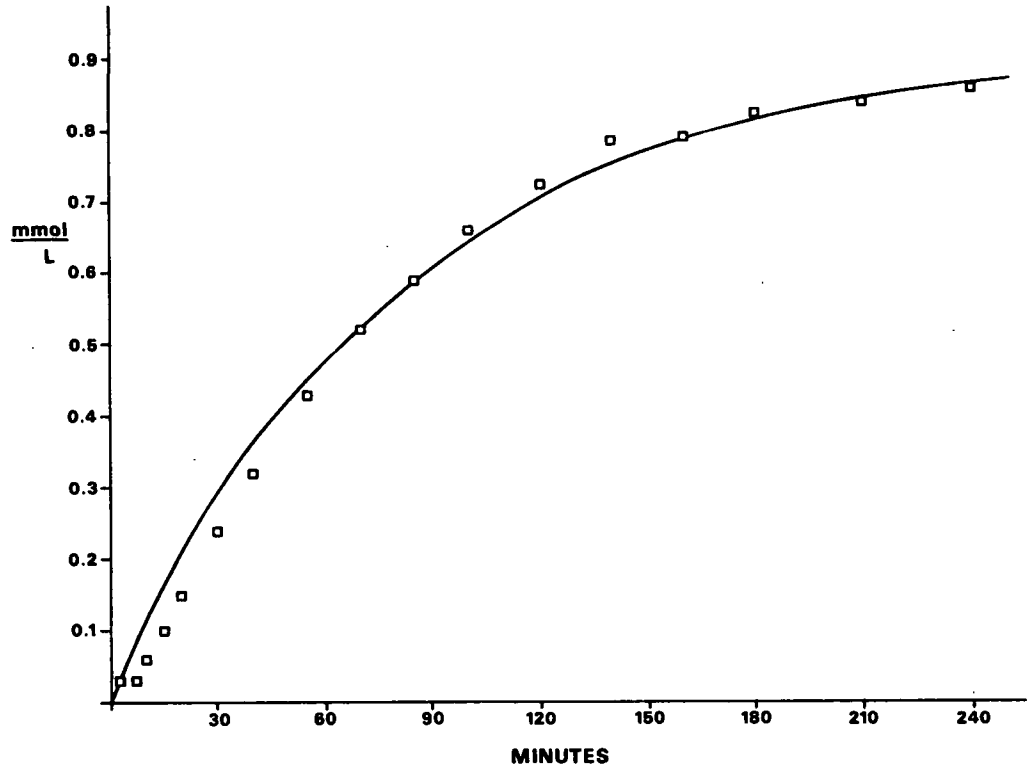
Figure 1. The concentration of syringyl alcohol (no additives) when it was reacted in 1N NaOH at 135°C for four hours.





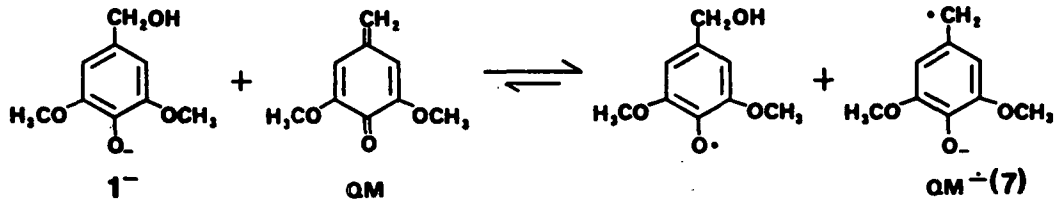
Figures 2 (top) and 3 (bottom). The concentrations of disyringylmethane (Fig. 2) and syringaldehyde (Fig. 3) when syringyl alcohol was reacted in 1N NaOH at 135°C for four hours.



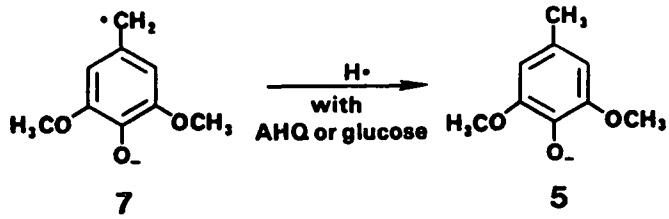


Figures 4 (top) and 5 (bottom). The concentrations of 4-methylsyringol (Fig. 4) and syringol (Fig. 5) when syringyl alcohol was reacted in 1N NaOH at 135°C for four hours.

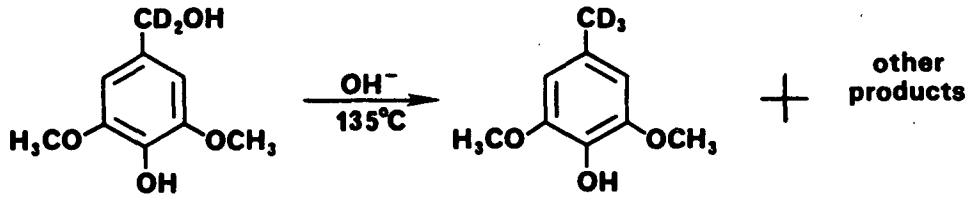
The mechanism responsible for the formation of 4-methylsyringol and bisyringyl is viewed as beginning with the transfer of an electron from a phenolate ion to a QM, resulting in a phenoxy radical and quinonemethide radical-anion ($QM^{\cdot-}$) **7**, as shown in Eq. (2). By obtaining a hydrogen atom, the $QM^{\cdot-}$ can form 4-methylsyringol [Eq. (3)]. Alternatively, the $QM^{\cdot-}$ can couple with either another $QM^{\cdot-}$ or with a QM followed by electron-transfer to form bisyringyl (Scheme 1).



(2)



(3)



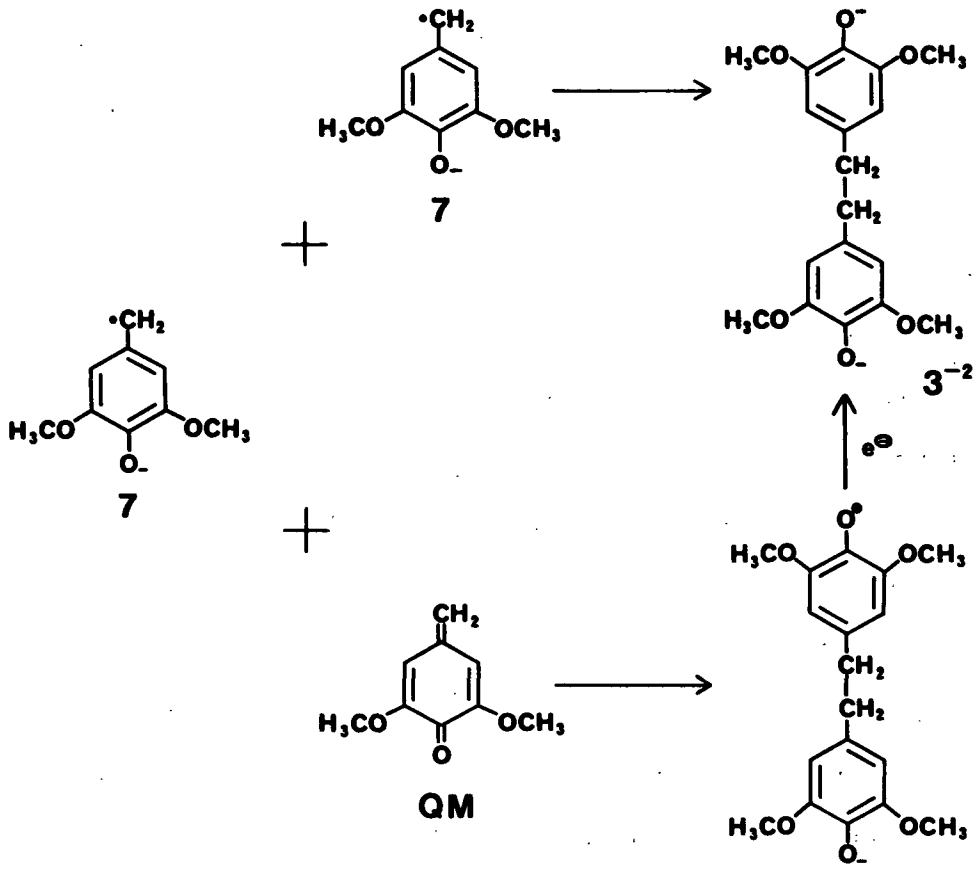
(4)

If 4-methylsyringol is formed by a radical mechanism, where does it obtain a hydrogen atom? A likely candidate is one of the benzylic hydrogens of syringyl alcohol. Reaction of α,α-dideuteriosyringyl alcohol in 1N NaOH at 135°C produced 4-methylsyringol containing three deuteriums [Eq. (4)] as determined by mass spectroscopy. The incorporation of a third deuterium confirms the source of hydrogen atoms as the benzylic position of syringyl alcohol.

RADICAL INITIATORS AND INHIBITORS

The production of 4-methylsyringol and bisyringyl shows that some of the reactions of syringyl alcohol are probably radical in nature. Could the production of disyringylmethane be at least partially, if not entirely, by a radical mechanism? In an attempt to answer this question, we looked at the effects of radical initiators and inhibitors on the alkaline reaction of syringyl alcohol.

Scheme 1. Formation of bisyringyl from a $QM^{\cdot-}$.



Radical Initiators

Two radical initiators, sodium persulfate and potassium ferricyanide, were added to syringyl alcohol condensation reactions. These initiators were added in the hope that they would convert phenolate ions to phenoxy radicals. Unfortunately, problems were incurred with both additives. Sodium persulfate

proved to be too good of an oxidizing agent, forming syringaldehyde very quickly (Fig. 6-10); the rate of disyringylmethane production was not increased.

Potassium ferricyanide produced a similar result (Fig. 6-10), rapid oxidation of syringyl alcohol to syringaldehyde, with no associated increase in the rate of disyringylmethane production. One point of interest with the addition of potassium ferricyanide was that the production of 4-methylsyringol began after 15 minutes and ended with a yield greater than the control (Fig. 9). Apparently, potassium ferricyanide initially generates an oxidative environment which is subsequently replaced by a reductive environment. But once again, the addition of an initiator, potassium ferricyanide, did not provide any useful information on the mechanism of disyringylmethane formation.

Radical Inhibitors

A known radical inhibitor, butylated hydroxytoluene (BHT), was added to a reaction of syringyl alcohol. By donating an electron (or hydrogen atom), BHT is able to quench radicals.[6] The t-butyl groups provide steric hindrance to make the BHT radical relatively stable. Although BHT is known to be insoluble in alkali at room temperature, its solubility at higher temperatures was unknown.[7] Unfortunately, BHT proved only sparingly soluble at 135°C. This was demonstrated by the withdrawal of samples from a solution reacting at 135°C. The samples were acidified, extracted with chloroform, and analyzed by gas chromatography. The peak area corresponding to BHT was very small when compared to a stock solution containing two molar equivalents of BHT. Apparently, the BHT floated on the surface of the reaction solution, which was observed when the reaction vessel was opened.

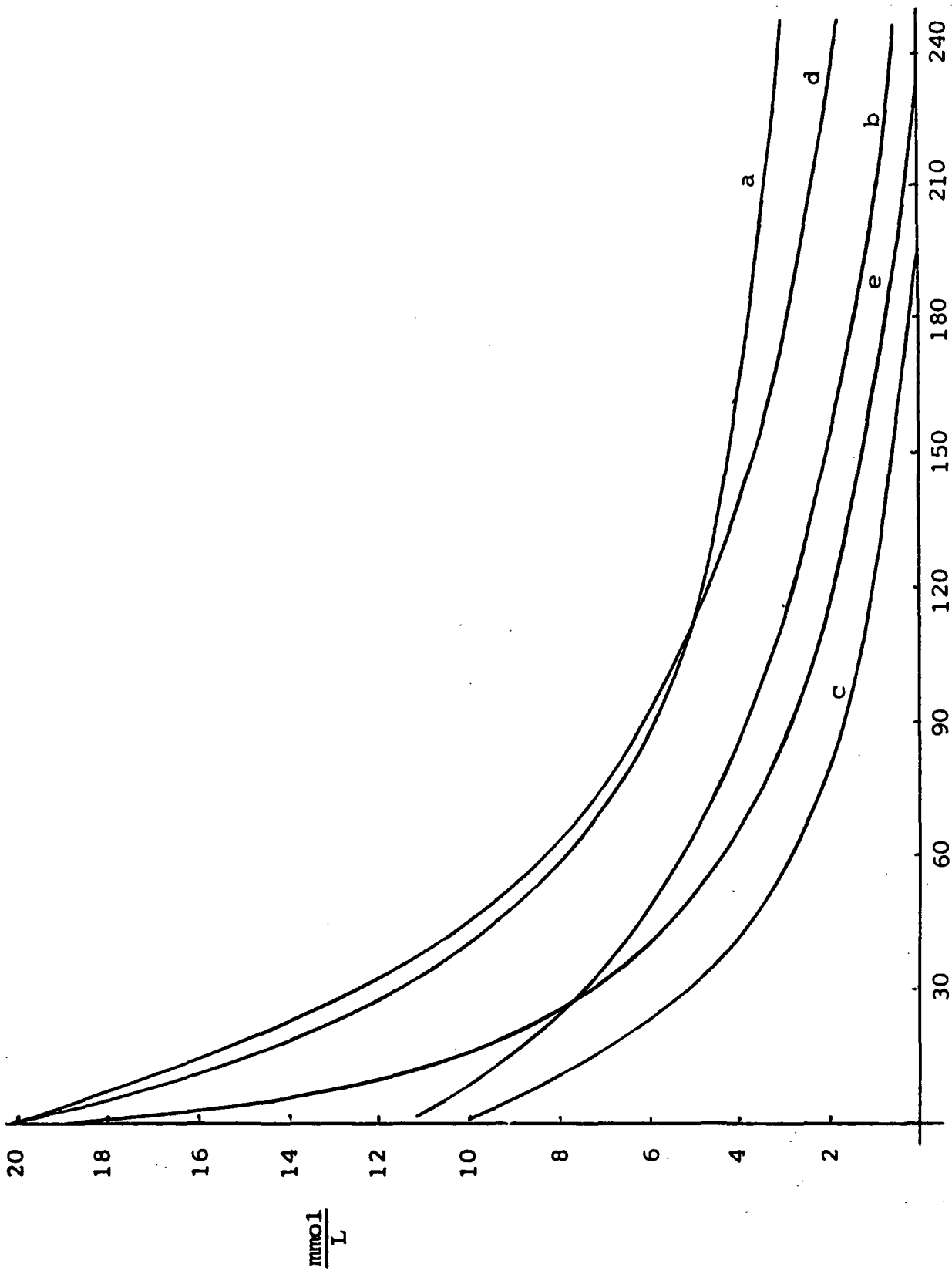
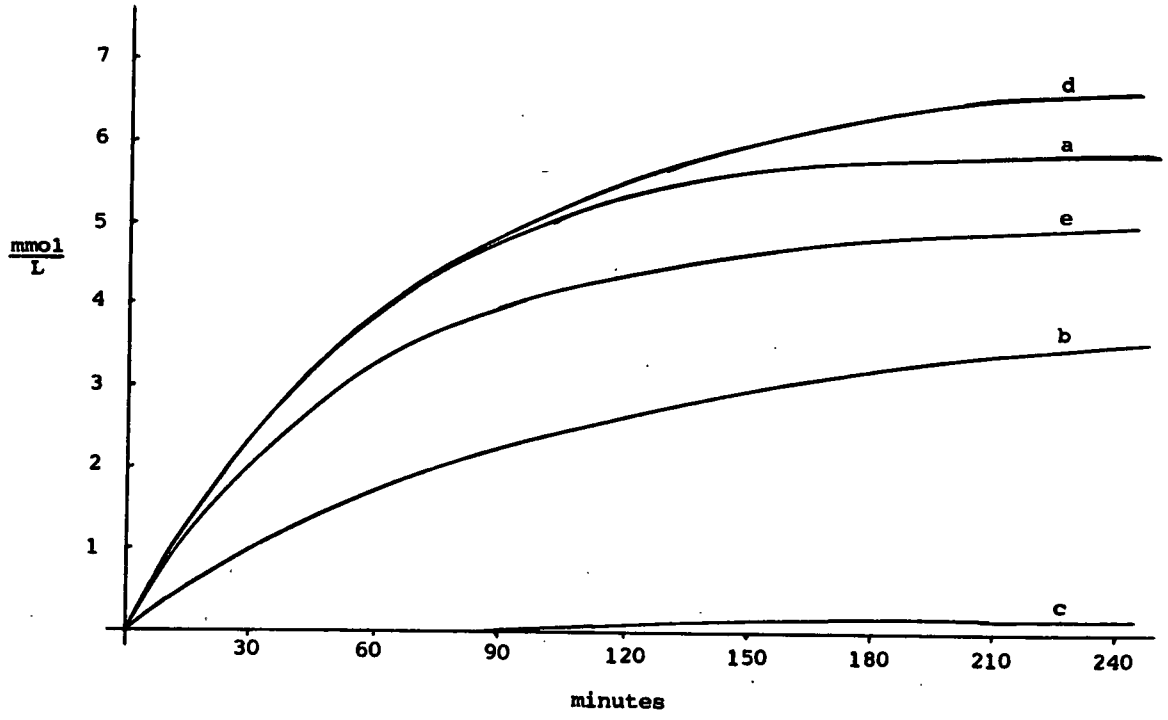
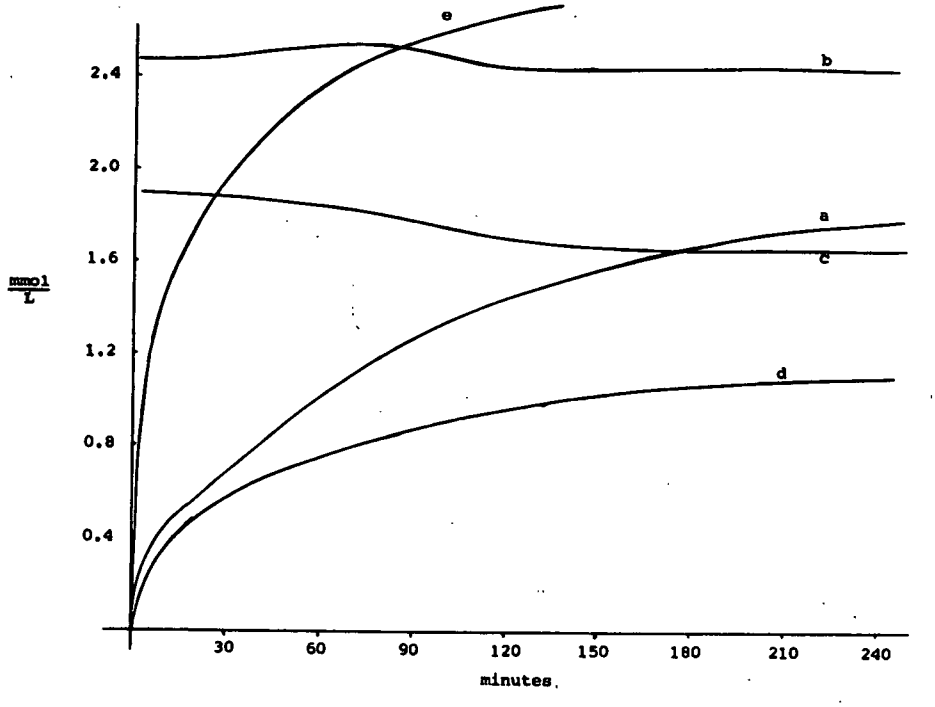
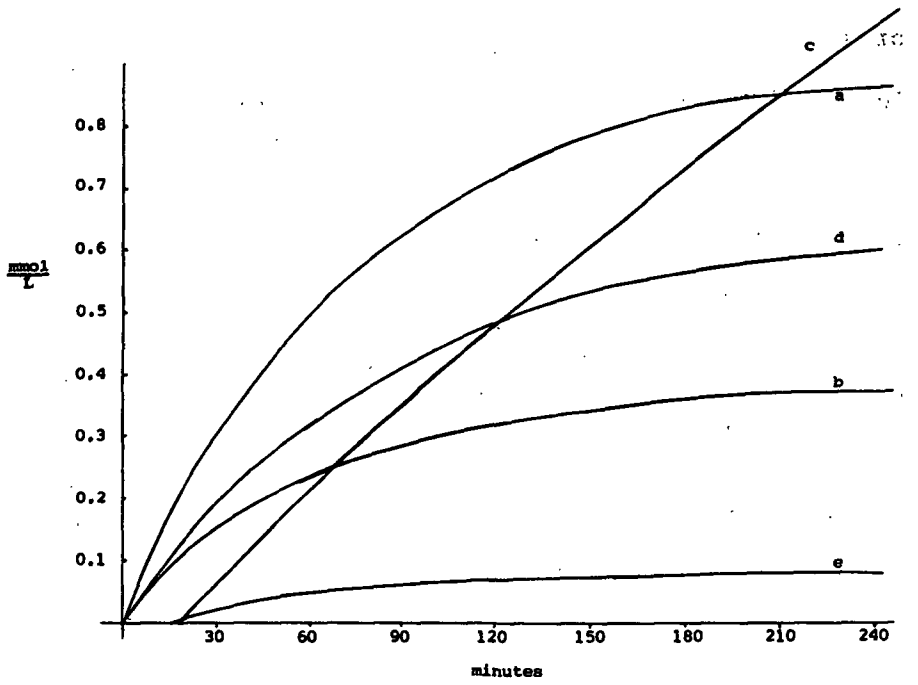


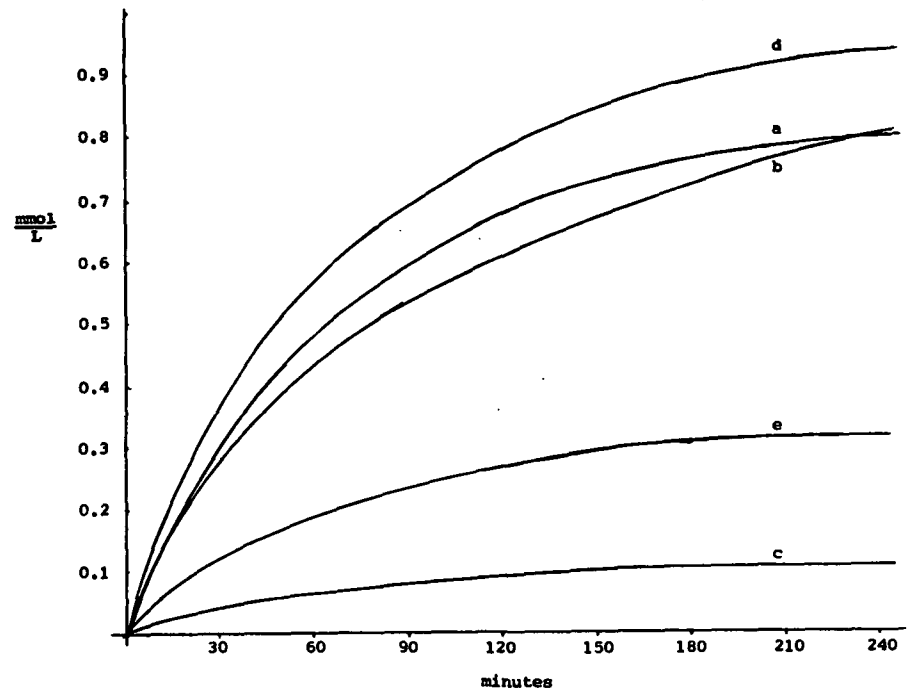
Figure 6. The concentration of syringyl alcohol through four hours in 1N NaOH at 135°C with the following additives: a - control (no additive), b - sodium persulfate, c - potassium ferricyanide, d - 2,4,6-trimethylphenol, and e - 3,5-dinitrobenzoic acid. The data points of the graphs were similar to those shown in Fig. 1.





Figures 7 (top) and 8 (bottom). The concentration profiles of disyringylmethane (Fig. 7) and syringaldehyde (Fig. 8) when syringyl alcohol was reacted in 1N NaOH at 135°C for four hours. For a-e, see Fig. 6. The data points of these graphs were similar to those shown in Fig. 2 and 3.



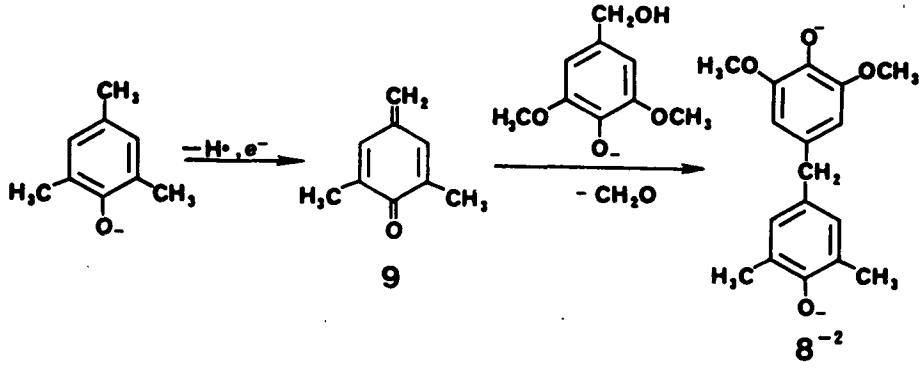


Figures 9 (top) and 10 (bottom). The concentration profiles of 4-methylsyringol (Fig. 9) and syringol (Fig. 10) when syringyl alcohol was reacted in 1N NaOH at 135°C for four hours. For a-e, see Fig. 6. The data points of these graphs were similar to those shown in Fig. 4 and 5.

A compound of good alkali solubility, 2,4,6-trimethylphenol, was added in two molar equivalents to a syringyl alcohol reaction. Trimethylphenol was used in the hope that, by donating electrons, it would quench reactive radicals. Although it lacks the steric hindrance of BHT, an excess of trimethylphenol could possibly quench reactive radicals, at least temporarily, and thus reduce condensation. However, addition of trimethylphenol had no effect on the reaction of syringyl alcohol (Fig. 6-10).

One point of interest with trimethylphenol addition was the formation of a minor compound with a molecular weight of 288. This mass number corresponds to a diphenylmethane dimer between syringyl alcohol and trimethylphenol. A logical structure is dimer **8**. Such a compound would be difficult to form by a traditional ionic mechanism; a radical mechanism appears more likely. To form **8**, a trimethylphenolate ion could lose an electron and a hydrogen atom (in any order) to give QM **9** (Scheme 2). Condensation of this QM with syringyl alcohol would give **8**. Thus, structures analogous to trimethylphenol, which are incapable of directly forming QMs, may still be able to do so by a two-step oxidation process.

Scheme 2. Possible formation of **8** from trimethylphenol and syringyl alcohol.



Previously, 3,5-dinitrobenzoic acid (DNBA) was observed to decrease the amount of dimers and trimers formed during the alkaline reaction of vanillyl alcohol.[4] By accepting electrons, dinitrobenzenes have been shown to quench radical-anions in $S_{RN}1$ reactions.[8] Addition of DNBA to a syringyl alcohol reaction, however, proved only to increase the production of syringaldehyde; the rate of disyringylmethane production was affected only by the fact that less syringyl alcohol was probably available for reaction. Apparently, syringyl alcohol donates electrons to DNBA and becomes oxidized to syringaldehyde. Therefore, the previous lower levels of condensation products observed with reactions of vanillyl alcohol and DNBA[4] appear to be due to the oxidation of reactive compounds to unreactive products (benzylic alcohols to aldehydes). This is consistent with the observed formation of oxidized dimers along with a greater formation of vanillin in the vanillyl alcohol study.

In summary, the inhibitors proved to be either insoluble or not suitable, and the initiators only oxidized syringyl alcohol to syringaldehyde. The trouble with initiators is that it may be difficult to find one which can generate a phenoxy radical without forming syringaldehyde. With inhibitors, it may be difficult to find one that can withstand the harsh conditions of the reaction. As a result of these problems, the mechanism of disyringylmethane formation remains unresolved.

PULPING REAGENTS

Previous studies have shown that AHQ and sodium sulfide were able to reduce condensation reactions.[4,5] An investigation into the mechanism(s) by which these compounds prevent condensation was performed by adding AHQ, glucose, and/or sodium sulfide to alkaline reactions of syringyl alcohol.

Anthrahydroquinone

Addition of two molar equivalents of AHQ to an alkaline reaction of syringyl alcohol resulted in a rapid increase in the rate of syringyl alcohol consumption and a drastic change in the product distribution (Fig. 11-16). Production of disyringylmethane was greatly retarded, while that of the electron-transfer products, 4-methylsyringol and bisyringyl, was enhanced.

As can be seen in Fig. 16, bisyringyl was formed rapidly in the first 15 minutes followed by no perceivable formation during the remainder of the reaction. Production of 4-methylsyringol, on the other hand, occurred throughout the reaction and its yield was more than three times that of the control (Fig. 14).

The production of a significant amount of bisyringyl (yield = 15%) and an increased production of 4-methylsyringol indicate that AHQ transferred electrons to syringyl QMs, forming QM$^{\bullet-}$s (**7**), a process detailed in Scheme 3. We speculate that the concentrations of QMs and QM$^{\bullet-}$s drop off to some low values after 15 minutes, resulting in the probability of a collision to give bisyringyl to also become low; this leaves the QM$^{\bullet-}$s with only one reaction, reduction via hydrogen atom abstraction to give 4-methylsyringol. (The production of bisyringyl was so low in the control and other syringyl alcohol/additive reactions that accurate concentration profiles for this product were not possible.)

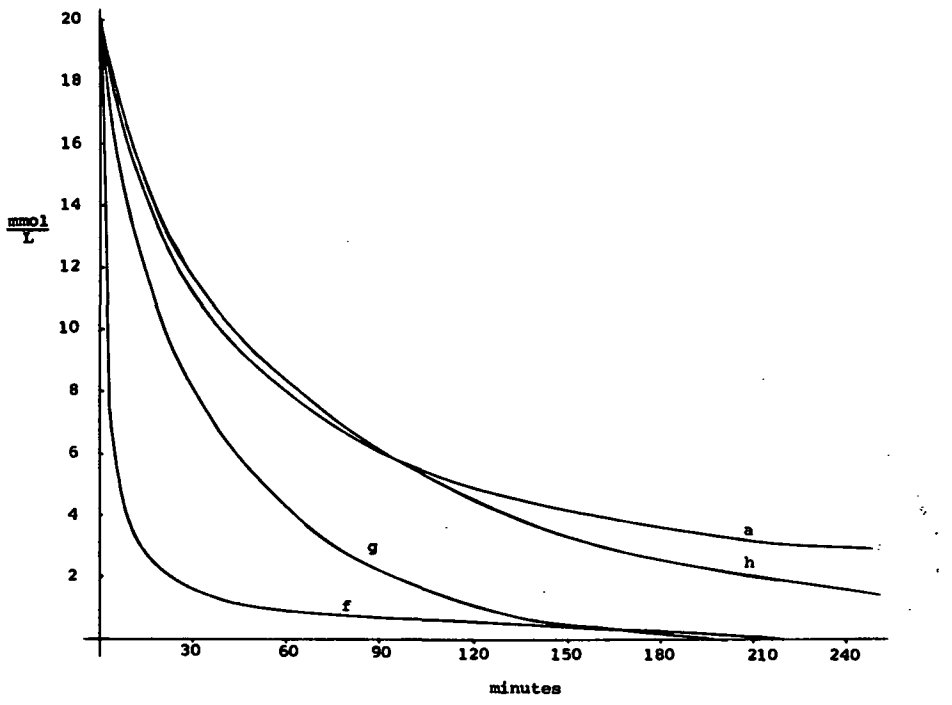
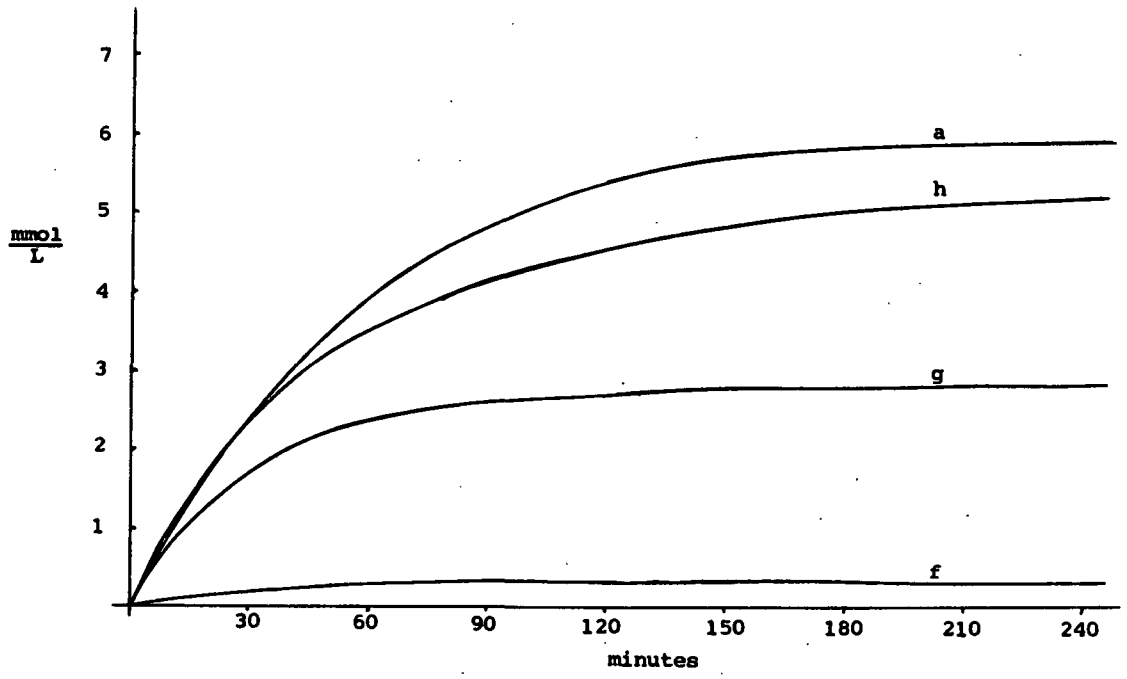
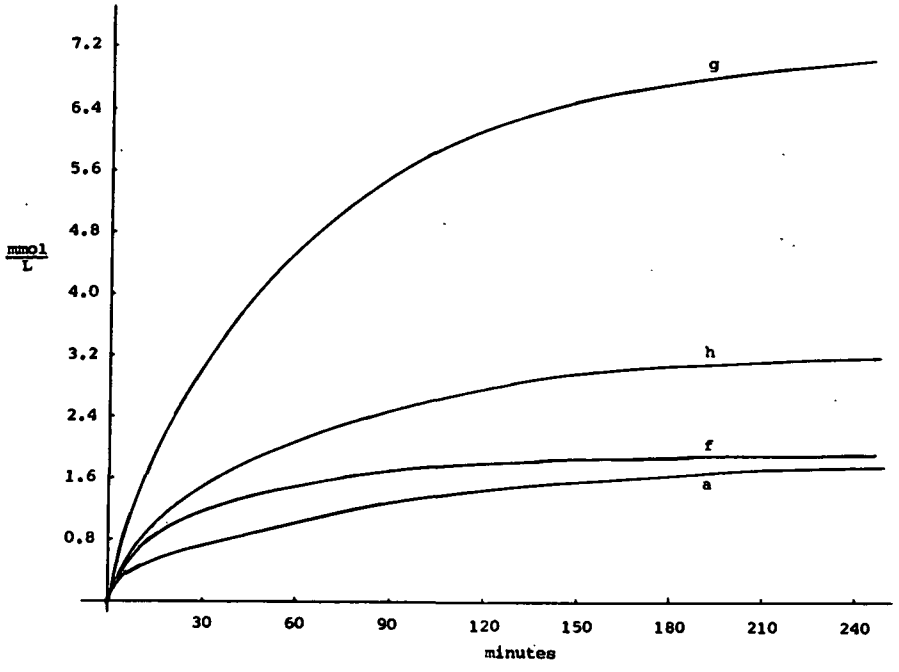
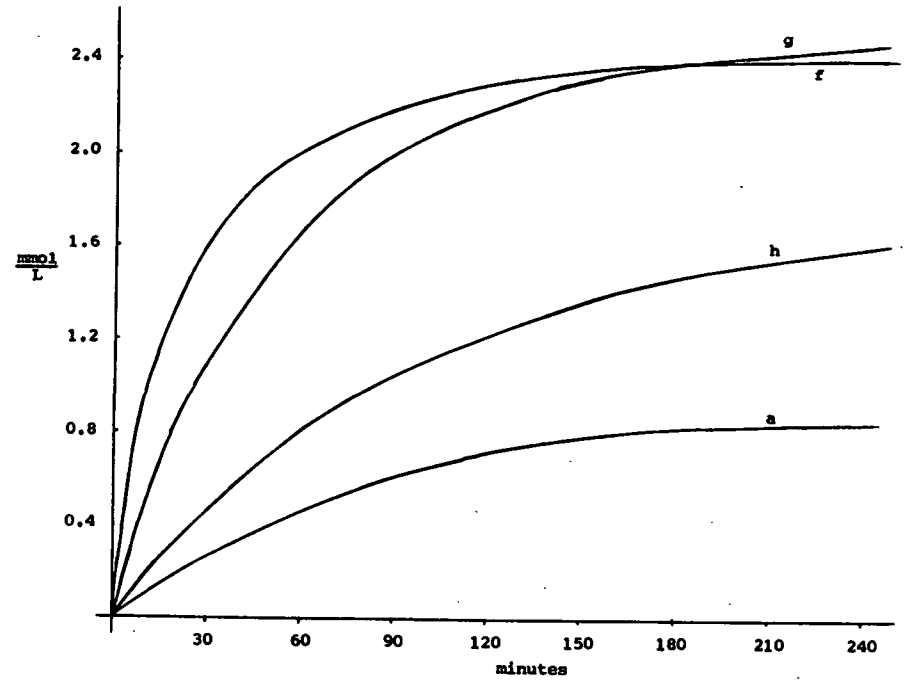


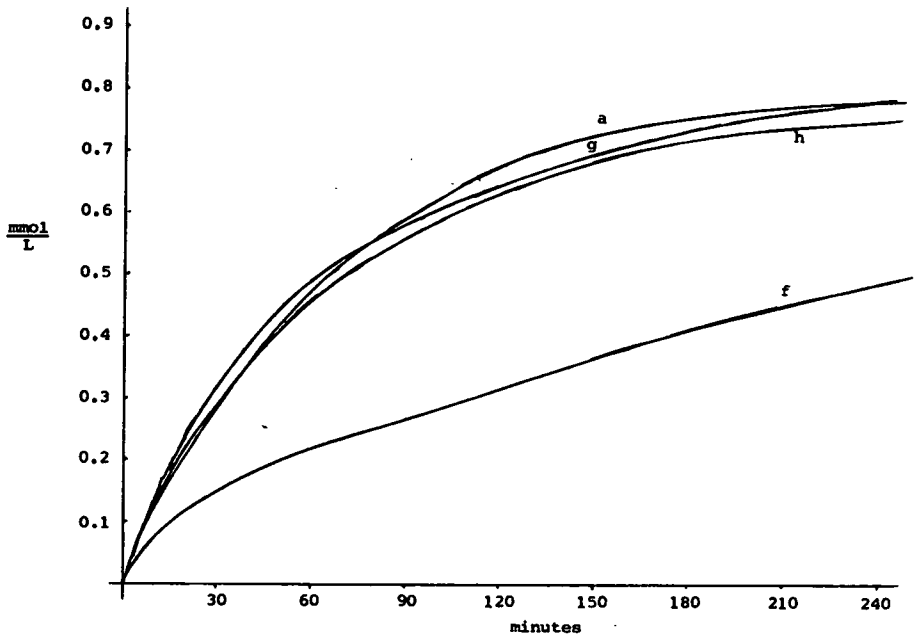
Figure 11. The concentration of syringyl alcohol through four hours in 1N NaOH at 135°C with various additions of AHQ. a - control (no additive), f - 2 molar equivalents, g - 0.5 molar equivalent, and h - 0.1 molar equivalent. The data points of the graphs were similar to those shown in Fig. 1.





Figures 12 (top) and 13 (bottom). The concentration profiles of disyringylmethane (Fig. 12) and syringaldehyde (Fig. 13) when syringyl alcohol was reacted in 1N NaOH at 135°C for four hours with various levels of AHQ. For a, f-h, see Fig. 11. The data points of these graphs were similar to those shown in Fig. 2 and 3.





Figures 14 (top) and 15 (bottom). The concentration profiles of 4-methyl-syringyl (Fig. 14) and syringol (Fig. 15) when syringyl alcohol was reacted in 1N NaOH at 135°C for four hours with various levels of AHQ. For a, f-h, see Fig. 11. The data points of these graphs were similar to those shown in Fig. 4 and 5.

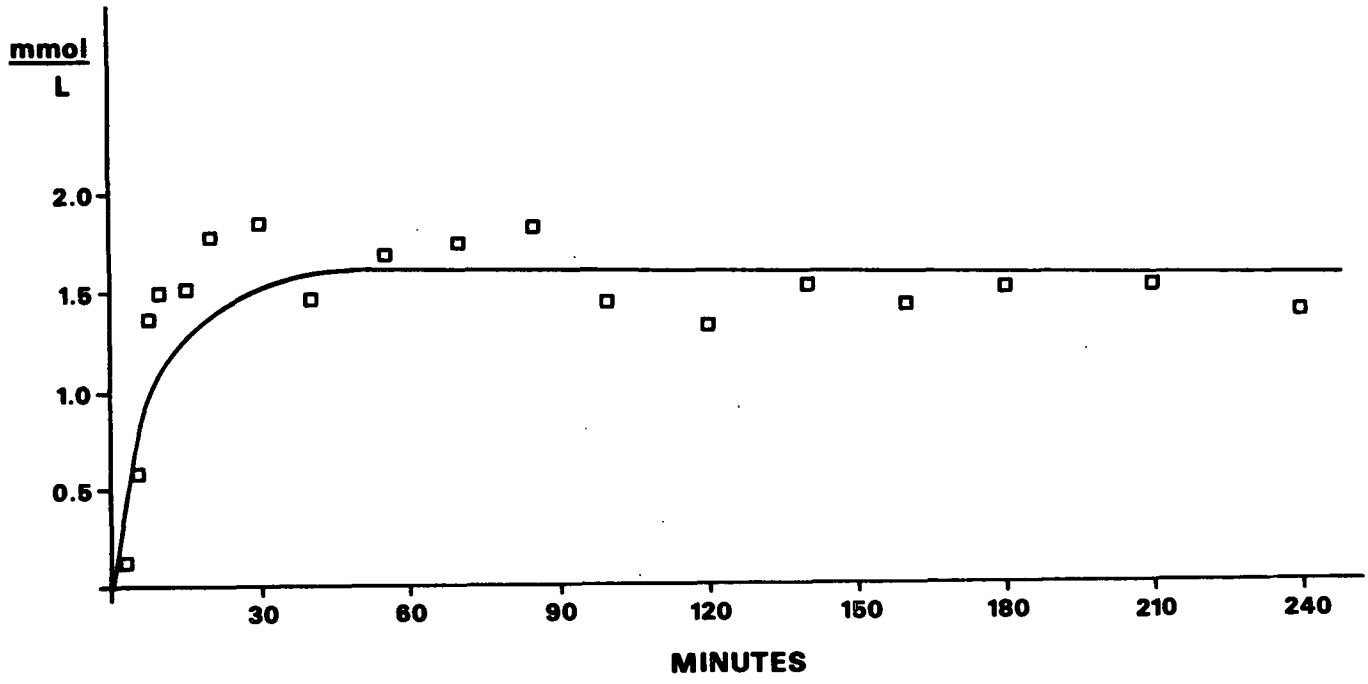
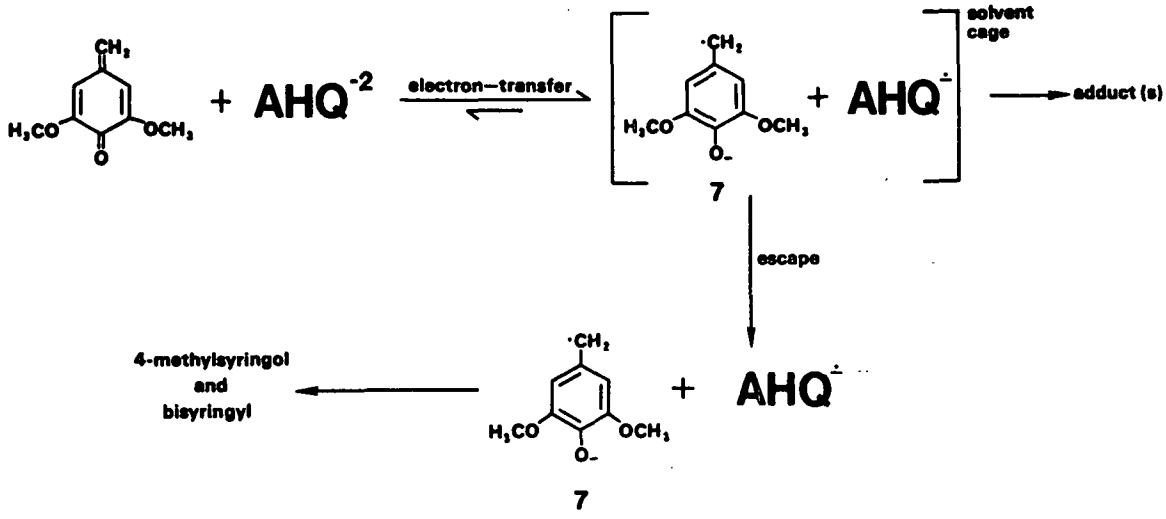


Figure 16. The concentration profile of bisyringyl when syringyl alcohol was reacted in 1N NaOH at 135°C with 2 molar equivalents of AHQ.

Scheme 3. Electron-transfer from AHQ to syringyl QMs - formation of 4-methylsyringol, bisyringyl, and AHQ-syringyl alcohol adducts.



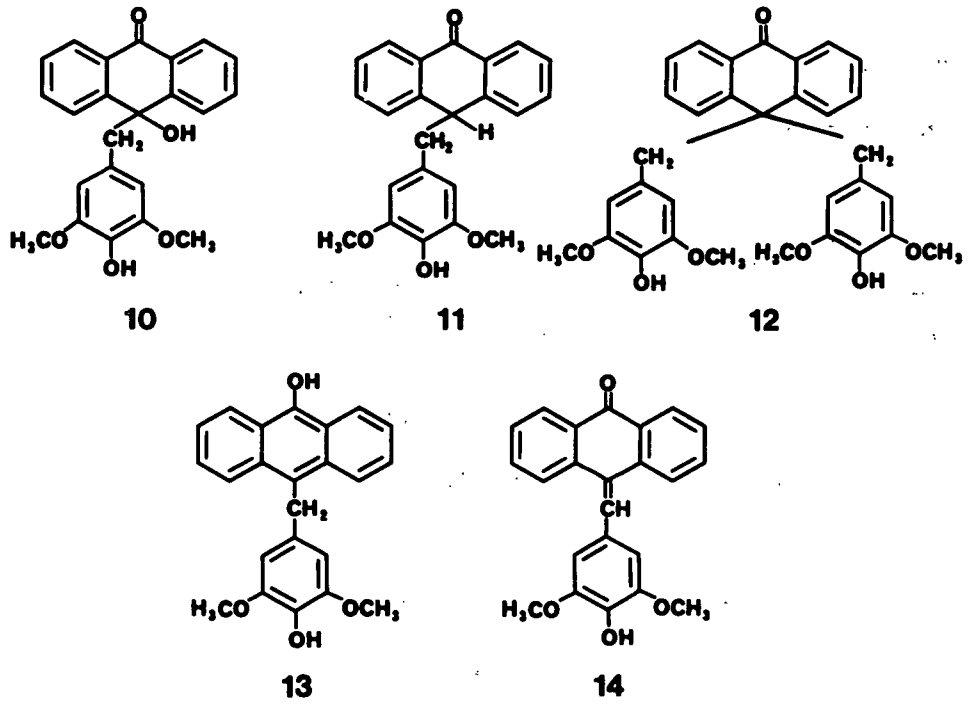
Five syringyl alcohol-AHQ adducts (**10**, **11**, **12**, **13**, and **14**) were identified as products of the reaction by gas chromatography/mass spectroscopy (GC/MS).

After five minutes, only adducts **10, 11,** and **12** were formed in significant amounts. However, all five of the adducts were observed as the reaction progressed beyond 20 minutes (Fig. 17).

Formation of adducts has been generally assumed to be by an ionic mechanism.[9-11] However, many electron transfer reactions are described as occurring in solvent cages.[12,13] Once electron transfer has taken place in a solvent cage, the radicals may form products within the cage or escape the cage and form other products. With AHQ electron transfer (Scheme 3), the product formed within the cage would be an adduct, while 4-methylsyringol and bisyringyl would be the products of the escaped radicals. Therefore, the formation of an adduct(s) could very well be part of the electron transfer reactions. Thus, the rapid rate of syringyl alcohol consumption with AHQ addition appears to be due to electron-transfer reactions forming $QM^{\bullet-}$s along with adducts.

Two other reactions of AHQ with syringyl alcohol were also examined; here the ratio of reactants was 0.5 and 0.1. Each of these low level AHQ additions increased the rate of syringyl alcohol consumption and decreased the rate of disyringylmethane production in proportion to their level of addition (Fig. 11 and 12).

The production of 4-methylsyringol (Fig. 14) was about twice as much for 0.1 eq. of AHQ as compared to the control, while for 0.5 eq. the production was equal to the 2 eq. addition. Very little bisyringyl was formed with these levels of AHQ. Apparently, the concentration of $QM^{\bullet-}$s never reached levels for good bisyringyl production. Consequently, the vast majority of the $QM^{\bullet-}$s formed 4-methylsyringol, allowing 0.5 eq. to produce as much as 2 eq.



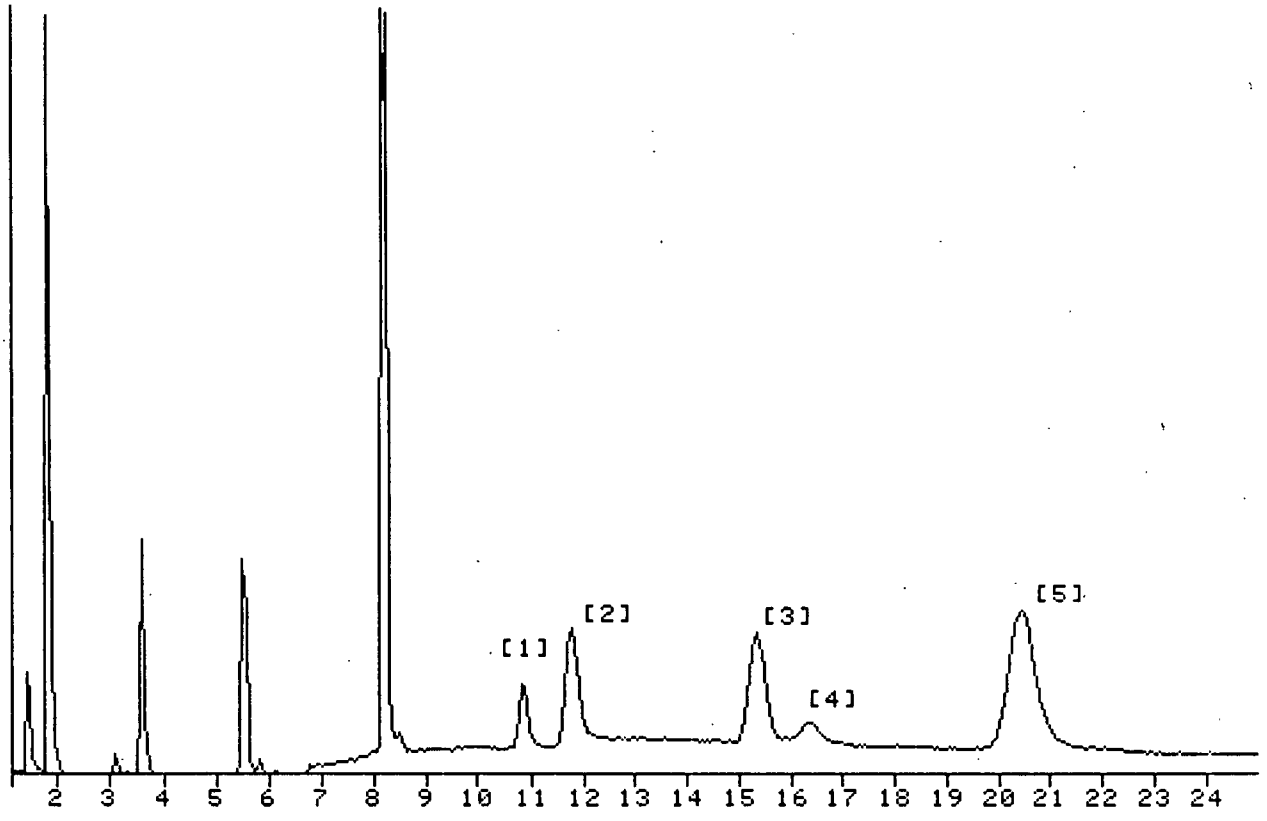


Figure 17. The GC/MS of the reaction of syringyl alcohol in 1N NaOH at 135°C with 2 molar equivalents of AHQ after four hours. Peak 1 - **10**, Peak 2 - **11**, Peak 3 - **13**, Peak 4 - **14**, and Peak 5 - **12**. The unnumbered peaks correspond to, from left to right, syringol, 4-methylsyringol, syringaldehyde, syringyl alcohol, AQ, and dimeric products. An expansion of the y-axis was done at 6.7 min resulting in the peaks thereafter appearing larger in comparison to the peaks before the expansion.

Syringaldehyde, however, did not follow the pattern of the other compounds; the 0.5 eq. AHQ addition produced relatively large amounts, and 0.1 eq. produced even more than 0.5 eq. (Fig. 13). Evidently, AHQ^{-2} reduces QMs, forming either $AHQ^{\bullet-}$ or AQ, which then oxidize syringyl alcohol to syringaldehyde. With 2 eq. of AHQ, the syringyl alcohol is almost completely consumed after 20 minutes; little is left to be oxidized to syringaldehyde. Thus, the lower levels of AHQ addition exhibited greater yields of 4-methylsyringol and syringaldehyde as compared to the control, but bisyringyl was once again present in only trace levels.

Glucose

The effect carbohydrates have on lignin condensation reactions was determined by the addition of two molar equivalents of glucose to the alkaline reaction of syringyl alcohol. As can be seen in Fig. 18, the consumption rate of syringyl alcohol was only slightly increased from the control. However, the production of disyringylmethane (Fig. 19) was less than half as much as the control. This decreased yield was probably due to reactions between syringyl alcohol and glucose, resulting in the formation of unidentified (condensed) products.

The importance of the glucose-syringyl alcohol condensation products was greatly enhanced with the addition of five molar equivalents of glucose (Fig. 18-22). With this reaction, syringyl alcohol consumption was very rapid, even greater than 2 eq. AHQ. Evidently, high levels of glucose cause the rapid formation of QM-carbohydrate condensation products, since the yields of the normally analyzed products, disyringylmethane, syringaldehyde, and syringol, were all very low. Only 4-methylsyringol showed an increase in yield as compared to the control reaction.

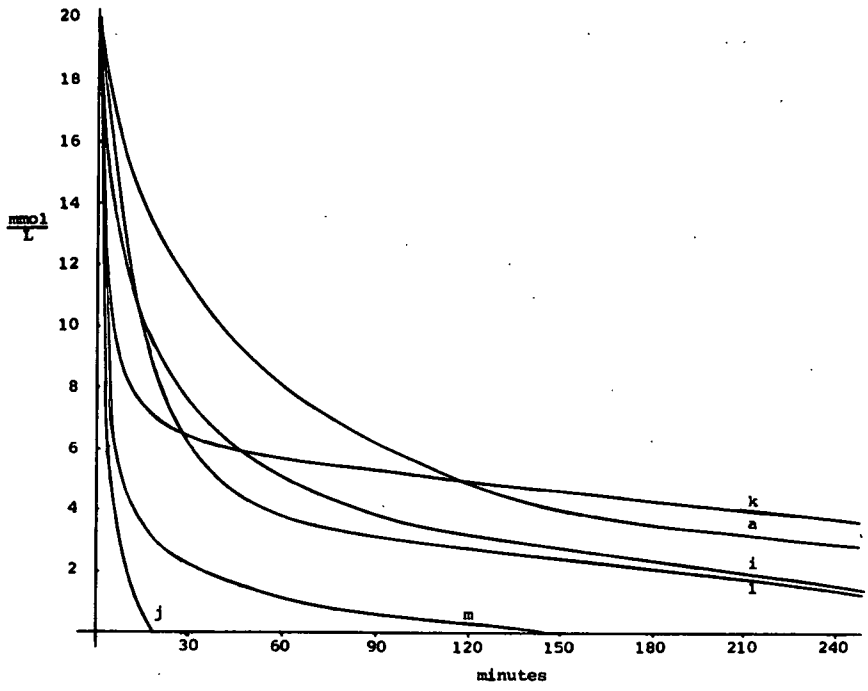
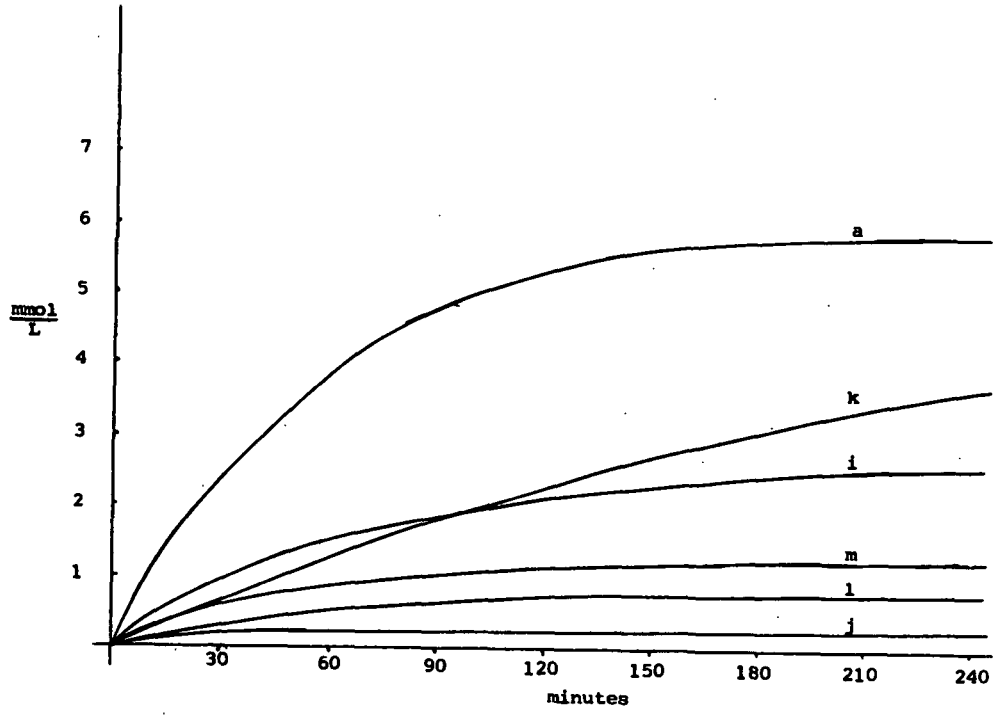
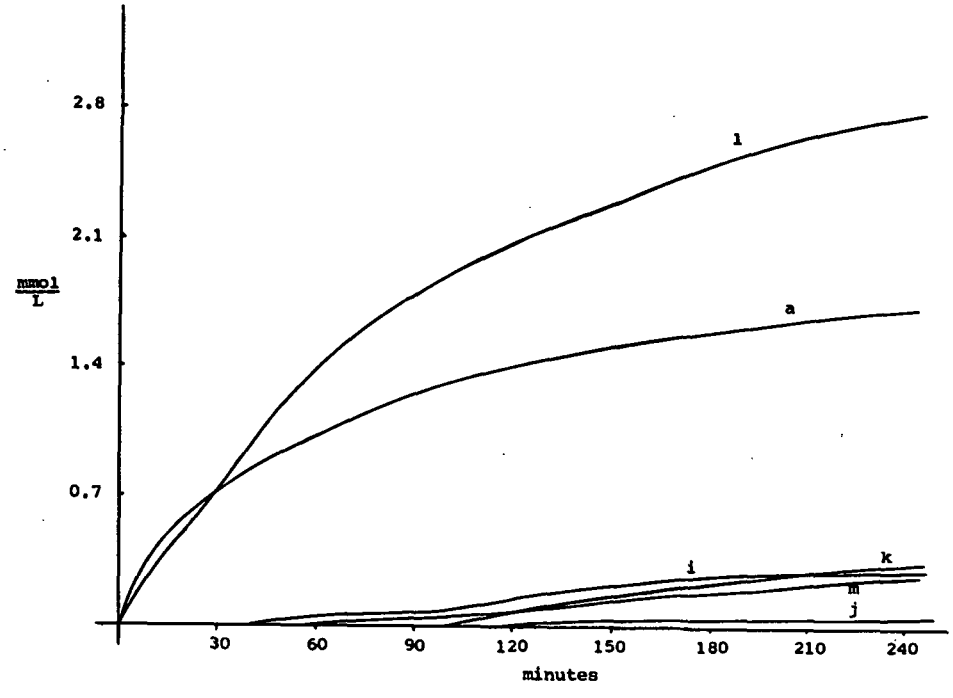
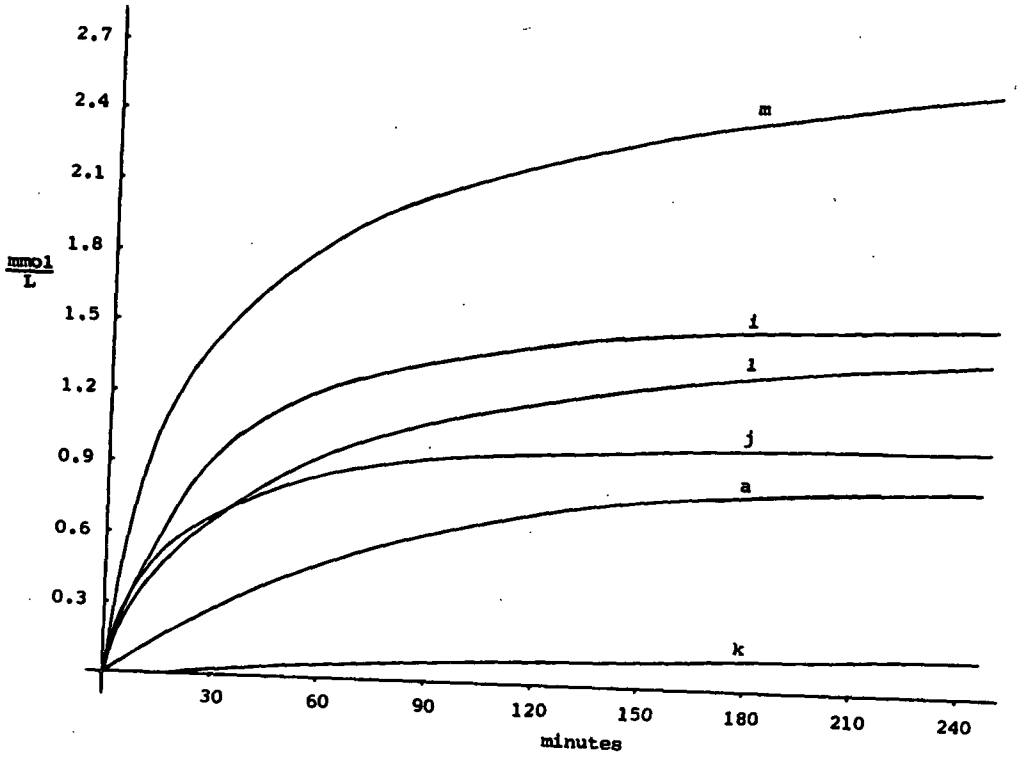


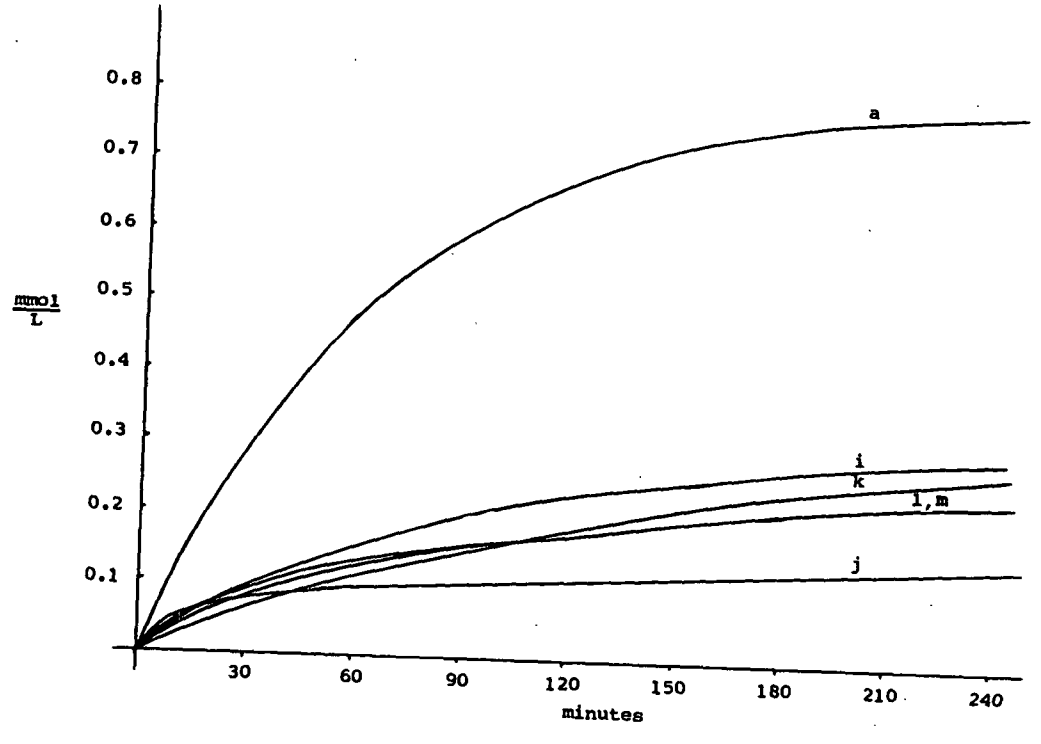
Figure 18. The concentration of syringyl alcohol through four hours in 1N NaOH at 135°C with the following additives: a - control (no additives), i - 2 molar equivalents of glucose, j - 5 molar equivalents of glucose, k - 2 molar equivalents of sodium sulfide, l - sodium sulfide and AHQ, and m - sodium sulfide and glucose. The data points of the graphs were similar to those shown in Fig. 1.





Figures 19 (top) and 20 (bottom). The concentration profiles of disyringylmethane (Fig. 19) and syringaldehyde (Fig. 20) when syringyl alcohol was reacted in 1N NaOH at 135°C for four hours with various additives. For a, l-m, see Fig. 18. The data points of these graphs were similar to those shown in Fig. 2 and 3.





Figures 21 (top) and 22 (bottom). The concentration profiles of 4-methylsyringol (Fig. 21) and syringol (Fig. 22) when syringyl alcohol was reacted in 1N NaOH at 135°C for four hours with various additives. For a, i-m, see Fig. 18. The data points of these graphs were similar to those shown in Fig. 4 and 5.

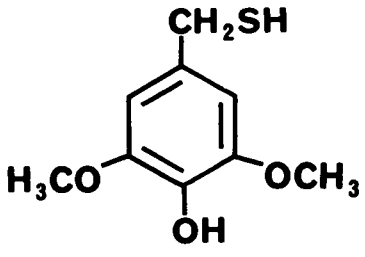
The 2 eq. addition of glucose increased the production of 4-methylsyringol even more than 5 eq. of glucose; the yield was almost double that of the control (Fig. 21). The increase in 4-methylsyringol indicates that glucose can also transfer electrons to QMs. Studies with a lignin model compound capable of detecting electron-transfer also demonstrated the ability of glucose to transfer electrons to QMs.[14] Thus, glucose can interfere with syringyl alcohol condensation either by transferring electrons to QMs or by forming glucose-syringyl alcohol products.

Sodium Sulfide

Addition of two molar equivalents of sodium sulfide to the reaction of syringyl alcohol produced an initial rapid consumption of syringyl alcohol for the first 20 minutes (Fig. 18). The remainder of the reaction was characterized by moderate consumption. As can be seen in Fig. 19, the initial rapid syringyl alcohol consumption was not accompanied by an increased production of disyringylmethane. Instead, disyringylmethane production was depressed throughout the reaction. But unlike the control reaction, where the production of disyringylmethane was essentially over in three hours, addition of sulfide resulted in the production of disyringylmethane at a rate which was still significant after four hours.

Addition of sulfide also decreased the production of the other products as well. As shown in Fig. 21, the production of 4-methylsyringol was less than a fourth of that produced in the control reaction. Evidently, sulfide was not interacting with syringyl alcohol by electron transfer, a conclusion which is supported by past research[3] and our other studies.[14]

An analysis of the reaction solution by GC/MS led to the identification of two products unique to sulfide addition. These products appear to be 3,5-dimethoxy-4-hydroxybenzylthiol (**15**) and di-(3,5-dimethoxy-4-hydroxybenzyl) sulfide (**16**). Previous investigations with vanillyl alcohol and sulfide at temperatures of 75-95°C provided di-(3-methoxy-4-hydroxybenzyl)sulfide (**17**) as the major product.[15] However, under the conditions of this study, sulfur compounds **15** and **16** were reactive intermediates and not the final products, as demonstrated in Fig. 23 and 24. They quickly form during the first 5-7.5 minutes of the reaction, after which their concentration slowly decreases.



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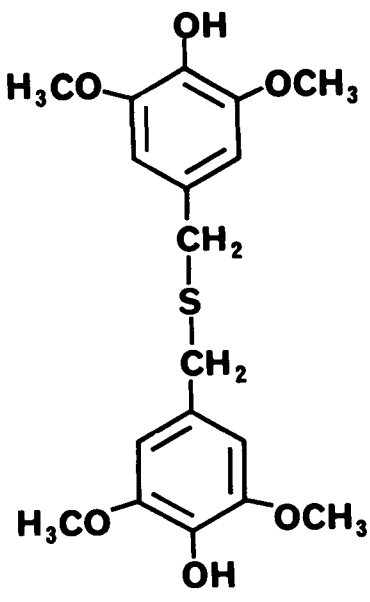

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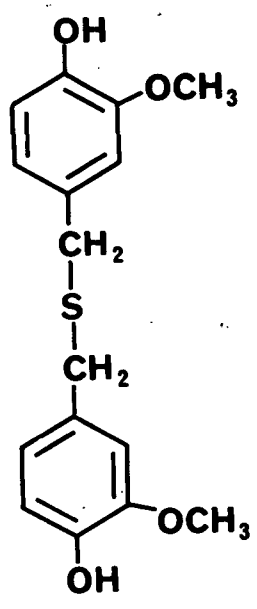

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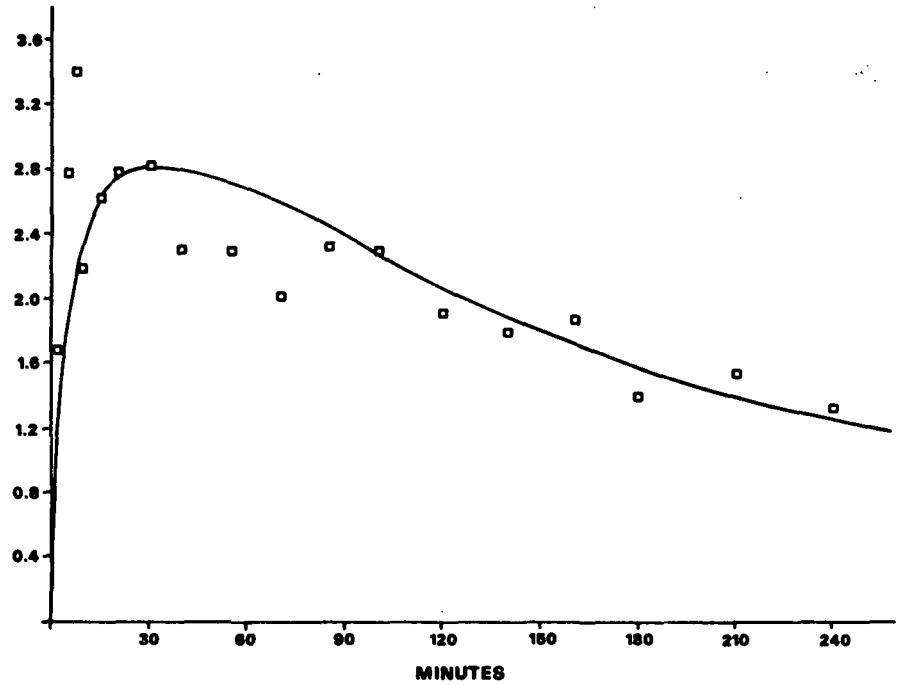
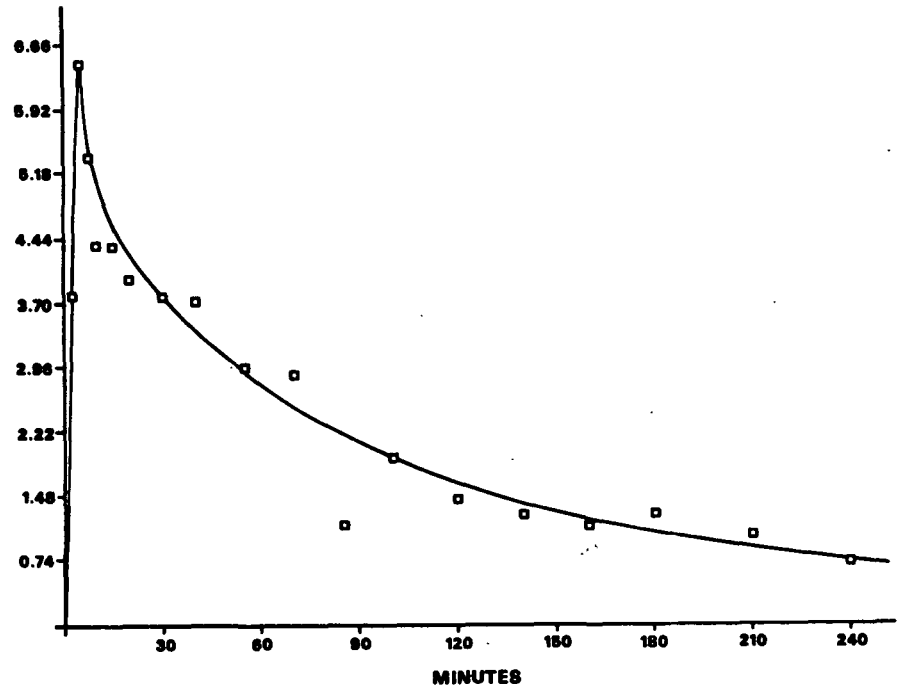
This behavior is substantiated when the concentrations of the compounds in Fig. 18-22 are added together on a monomer scale and plotted through the course of the reaction (Fig. 25). Initially, there is a rapid decrease in the total concentration during the first 20 minutes of the reaction due to the formation





Figures 23 (top) and 24 (bottom). The relative concentrations of benzylsulfide **15** (Fig. 23) and dibenzylsulfide **16** (Fig. 24) when syringyl alcohol and 2 molar equivalents of sodium sulfide were reacted in 1N NaOH at 135°C for four hours. The y-axes are the ratios of the GC area of **15** to the GC area of deuterated syringaldehyde per mole per liter (Fig. 23) and the GC area of **16** to the GC area of deuterated disyringylmethane per mole per liter (Fig. 24).

of **15** and **16**, which are not part of the material balance. After 20 minutes, the material balance shows an increase through the remainder of the reaction due to the consumption of **15** and **16** to the stable products in Fig. 19-22.

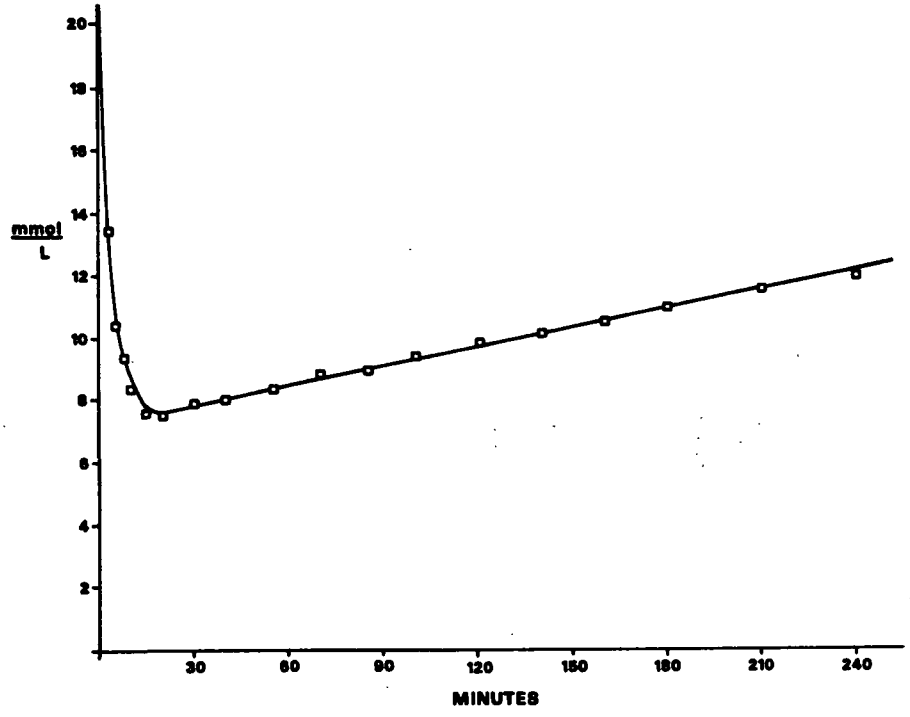
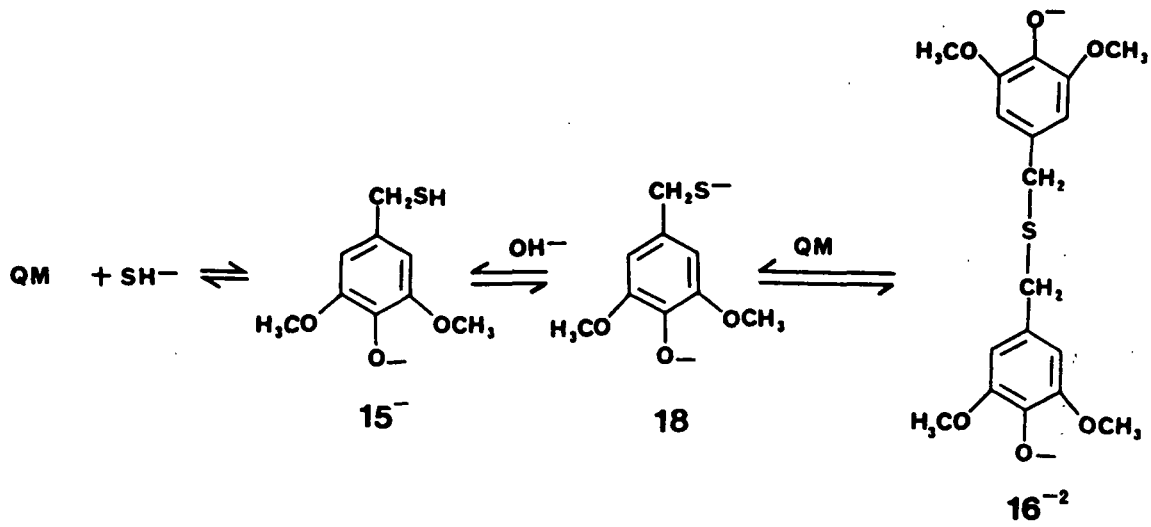


Figure 25. The material balance for the compounds of Fig. 18-22 when 2 molar equivalents of sodium sulfide were added to a reaction of syringyl alcohol in 1N NaOH at 135°C.

The production of **15** and **16** and their concentration profiles during the reaction, the material balance of the analyzed compounds, and the patterns of syringyl alcohol disappearance and disyringylmethane formation indicate that hydrosulfide reversibly bonds with syringyl QMs to initially form benzylthiol **15** (Scheme 4). (Under the conditions of the study, sulfide was probably present as hydrosulfide.[16-20]) With the alkalinity employed, benzylthiol **15** should be

easily ionized to a dianion **18**. Addition of benzylthiol dianion **18** to a second QM produces dibenzylsulfide **16**. Benzylthiol dianion **18** is possibly less reactive than syringyl alcohol toward producing QMs, since S^{-2} is in all likelihood a poorer leaving group than OH-. Thus, addition of sulfide produces compounds more stable to condensation.

Scheme 4. The ionic interaction of hydrosulfide with syringyl QMs.



The formation of these sulfur compounds should, however, be reversible. Therefore, during the first 20 minutes of the reaction, the equilibrium between syringyl alcohol and the two sulfur compounds was being established. After 20 minutes, as syringyl alcohol was being consumed to mostly disyringylmethane, the equilibrium shifted in the reverse direction, replenishing the syringyl alcohol. Consequently, only moderate consumption of syringyl alcohol was observed for the remainder of the reaction. Thus, sulfide inhibits the condensation of syringyl alcohol by a reversible ionic pathway in which addition of hydrosulfide to QMs produced "adducts." These "adducts" are more stable to condensation as compared to syringyl alcohol. This conclusion is in agreement with previous investigations.[15,21]

Sodium Sulfide-Anthrahydroquinone

One molar equivalent of sodium sulfide and AHQ were added to a reaction of syringyl alcohol to determine how the additives would compete for QMs. As expected with the addition of these compounds, the concentration of syringyl alcohol dropped rapidly for the initial 40 minutes (Fig. 18). The remainder of the reaction, however, was characterized by moderate losses of syringyl alcohol. The transition between these two phases, however, was not as abrupt as was observed with 2 eq. of sodium sulfide. The final concentration of syringyl alcohol was less than that obtained with 2 eq. of sodium sulfide but more than with 2 eq. of AHQ.

As for the concentration of the products (Fig. 19-22), disyringylmethane was produced in a sixth of that observed with the control, which was an amount somewhat greater than addition of 2 eq. AHQ. The yield of syringaldehyde was twice as much as for the control, and the amount of 4-methylsyringol produced was less than the addition of 0.1 eq. AHQ.

Apparently, sulfide is able to react with QMs faster than AHQ^{-2}. This conclusion is based on (a) the similarity between the disappearance of syringyl alcohol with the addition of only sulfide and (b) the fact that the observed yield of 4-methylsyringol was lower than that observed with the addition of 0.1 eq. of AHQ. Thus, what appears to be occurring is that sulfide interacts with syringyl alcohol by a reversible ionic pathway to establish the equilibrium between syringyl alcohol and sulfur compounds **15** and **16**. The remaining syringyl alcohol reacts with AHQ^{-2} to form 4-methylsyringol and adducts.

Sodium Sulfide-Glucose

Glucose was added in conjunction with sodium sulfide to observe the ability of glucose to electron-transfer in the presence of sulfide. The level of both

compounds was two molar equivalents. With this additive combination (Fig. 18-22), syringyl alcohol was quickly consumed. Production of disyringylmethane was similar to that of sulfide-AHQ. Syringaldehyde was also produced in low levels. However, formation of 4-methylsyringol was as good as 2 eq. of AHQ. Apparently, sulfide does not prevent glucose from undergoing electron-transfer reactions, but in fact assists glucose to generate good yields of the electron-transfer product, 4-methylsyringol.

CONCLUSIONS

The reaction of syringyl alcohol in 1N NaOH at 135°C produced two apparently radical derived products, 4-methylsyringol and bisyringyl. Addition of AHQ and glucose increased the yield of the radical derived products. Presumably, this increase was due to the transfer of an electron from AHQ^{-2} or glucose to a syringyl QM, resulting in a radical intermediate (a $QM^{\cdot -}$) which subsequently formed 4-methylsyringol and bisyringyl.

When sulfide was added, the consumption of syringyl alcohol occurred in two phases. The first phase was characterized by a rapid decrease in the syringyl alcohol concentration due to the establishment of an equilibrium between hydrosulfide ions and syringyl alcohol with QM-SH adducts. The second phase was characterized by only a moderate decrease in the syringyl alcohol concentration due to the equilibrium shifting in the reverse direction to replenish the syringyl alcohol consumed in the production of disyringylmethane. Thus, sulfide interacted with syringyl alcohol by a reversible ionic mechanism, while AHQ and glucose interacted by electron-transfer.

The addition of radical inhibitors and initiators to the alkaline reaction of syringyl alcohol did not provide useful information as to the extent of radical condensation of syringyl alcohol; this was due to various problems encountered with these additives.

EXPERIMENTAL

Proton and carbon-13 NMR spectra were recorded on a Jeol FX 100 spectrometer using $CDCl_3$ as the solvent and TMS as an internal standard. Gas chromatography (GC) analyses of samples were done with a Hewlett Packard 5840 GC chromatogram using either a two foot OV-17 (3%) on gas-chrom Q or a six foot 3% silicone OV-17 on 100/120 chromosorb W-HP MAOT-350; detection was by a Hewlett Packard 5985 mass spectrometer. The all glass system employed helium (30 mL/min) as the carrier gas, a jet separator at 250°C, a source temperature of 200°C, and an ionization voltage of 70 eV for the electron impact mode.

Oxygen-free water was prepared by boiling distilled water for about 30 min, after which nitrogen was dispersed into the water as it cooled to room temperature. After cooling, the water was sealed until needed.

Compounds obtained from the Aldrich Chemical Co., Milwaukee, Wisconsin, were syringaldehyde, syringol, lithium aluminum deuteride, and syringic acid. Ultrapure sodium hydroxide was obtained as a 30% solution from Alfa Products, Danvers, Massachusetts. Silica gel 60 (70-230 mesh ASTM) was used in all chromatographic separations.

PROCEDURES AND ANALYSES

Syringyl Alcohol Reaction (Control)

The reaction vessel, described in detail elsewhere,[22] consisted of a 250 mL capacity, Teflon-lined brass reactor which contained an inlet port for the introduction of starting materials and an outlet port for the sampling of the reaction solution. Stirring was by an external air driven magnet which turned a magnetic stirring bar in the reaction vessel.

The preparation of the reaction solutions was done in a nitrogen atmosphere. To the reaction vessel was added 128.32 g of oxygen-free water and 19.80 g of 30% ultrapure NaOH. Syringyl alcohol (0.5526 g, 0.0030 g mole) was dissolved in 4.50 g of oxygen-free water and 0.60 g of 30% ultrapure NaOH. This solution was then drawn into a Teflon tube (OD 1/8-inch, ID 1/16-inch). Into another Teflon tube was drawn 2.90 g of oxygen-free water. The syringyl alcohol solution, followed by the oxygen-free water, was connected to the reaction vessel by a slider injection valve (LDC/Milton Roy, Riviera Beach, Florida). The reaction vessel was placed in a 135°C oil bath and heated to temperature. Introduction of the syringyl alcohol solution was done with nitrogen at 100 psig. The final reaction solution had a volume of 150 mL (assuming a density of 1 g/mL) and a syringyl alcohol concentration of 0.020 mole/L.

A second slider injection valve with Teflon tubing was used for periodic sampling during the four hours of the reaction. Samples (~ 1.5 mL) were expelled from the sample valve into preweighed 4-mL glass vials and the weight of the samples was obtained. The density of the reaction solution was found to be 1.044 g/mL (average of five 10-mL solutions), allowing the volumes of the samples to be determined. To the samples was added approximately 0.15 g of a standard solution containing 3.8 g of oxygen-free water, 0.55 g of 30% ultrapure NaOH, and the following amounts of deuterium-enriched compounds: 0.0740 g syringyl alcohol, 0.0213 g disyringylmethane, 0.0100 g syringaldehyde, 0.0067 g 4-methylsyringol,[23] and 0.0025 g syringol. The samples were acidified with 2M H_2SO_4 until a precipitate was observed and then extracted with 1.0 g of chloroform.

Analysis of the reaction samples was done by using the Selective Ion Monitoring System (SIMS) of the mass spectrometer. Only specific ions are

recorded using SIMS and not the entire mass spectrum. Thus, the compounds were separated by GC and the ions representing the molecular weights of the deuterated and nondeuterated compounds were recorded. (For deuterium-enriched syringol, 156 was used rather than 157, as 156 gave a greater area.)

Just prior to each SIMS analysis, eight standard solutions of known molar ratios of deuterated to nondeuterated syringol, 4-methylsyringol,[23] syringaldehyde, syringyl alcohol, and disyringylmethane also were analyzed by the SIMS technique; a standard response factor curve for each compound was obtained. The areas of the molecular weight ions were measured, allowing the concentration at the time of sampling to be calculated for each compound from the observed peak ratios for the nondeuterated and deuterated compounds [for example: peak area of syringyl alcohol (184.1)/peak area of deuterium-enriched syringyl alcohol (186.1)] and the response factor curves.

Syringyl Alcohol Additive Reactions

The additive reactions were prepared in the same manner as the control reaction. Some of the additives were placed in the reaction vessel; these included sodium sulfide (0.4683 g, 2 molar equivalents), AHQ (see below), butylated hydroxytoluene (1.3218 g, 2 molar equivalents), 2,4,6-trimethylphenol (0.8171 g, 2 molar equivalents), and 3,5-dinitrobenzoic acid (0.1909 g, 0.3 molar equivalent).

The other additives were added as solutions to the reaction vessel simultaneously with syringyl alcohol. The amount of oxygen-free water necessary to dissolve these additives was subtracted from that added to the reaction vessel. The additives added as solutions include glucose (1.0810 g, 2 molar equivalents, 5.00 g water or 2.7024 g, 5 molar equivalents, 12.50 g water), sodium persulfate

(0.2143 g, 0.3 molar equivalent, 4.25 g water), and potassium ferricyanide (1.9756 g, 2 molar equivalents, 5.50 g water). Sampling and analysis for the additive reactions was done in the same manner as the control.

Bisyringyl Analysis

The concentration of bisyringyl from the syringyl alcohol reaction with 2 eq. AHQ was determined by GC analysis of the reaction samples. The GC used was a Hewlett Packard 5890 with a flame ionization detector. The six foot OV-17 column was used with 30 mL/min of helium (carrier gas) and a temperature program of 210-285°C at 15°/min holding at 285 for four min, 285-275° at 30°/min holding at 275 for 1.25 min, and finally, 275-300°C at 30°/min holding at 300 for three min. For an internal standard, the deuterium-enriched disyringylmethane was used. The assumption was made that disyringylmethane and its deuterium-enriched analog had the same response factor. This assumption allowed for the subtraction of the nondeuterated portion of the disyringylmethane peak; the concentration of nondeuterated disyringylmethane in the reaction samples was previously determined by SIMS. The eight SIMS standard solutions, which also contained bisyringyl of varying amounts, were used to obtain a response factor curve for deuterium-enriched disyringylmethane and bisyringyl.

Syringyl Alcohol-AHQ Adducts

To investigate the adducts formed between syringyl alcohol and AHQ, a reaction solution was prepared and done exactly as the previously described 2 molar equivalent AHQ addition except that only nine samples were withdrawn through the course of the four-hour reaction. Each sample (~ 3 mL) was methylated by adding, with stirring, 1 mL of dimethylsulfate. After 15 min, the excess dimethylsulfate was quenched with 4.5 mL of concentrated NH_4OH and the methylated sample was then extracted with chloroform. The samples were qualitatively

analyzed by the Hewlett Packard 5890 with an OV-17 column and the adducts were identified by GC/MS:[24] m/e (%)

10 404 (M^+, 1.0), 223 (13.5), 182 (11.2), 181 (100.0).

11 374 (M^+, 1.4), 192 (3.5), 182 (11.4), 181 (100.0).

12 389 (29.1), 388 (100.0), 373 (46.3), 345 (29.7), 221 (17.1), 202 (38.6), 101 (35.1).

13 389 (29.0), 388 (M^+, 100.0), 374 (13.6), 373 (56.3), 311 (10.5), 255 (10.1), 221 (10.5), 215 (11.5), 207 (11.6), 178 (23.8), 163 (17.5), 122 (12.1), 119 (11.1), 133 (16.3).

14 373 (17.4), 372 (100.0), 357 (30.0), 297 (31.4), 213 (19.8), 171 (26.4).

Sulfur Compounds

The qualitative concentration analysis of the sulfur products formed from the addition of 2 molar equivalents of sodium sulfide to an alkaline reaction of syringyl alcohol was accomplished by obtaining GC chromatograms for the 18 reaction samples with the Hewlett Packard 5890 using the OV-17 column. As with the analysis of bisyringyl, the assumption was made that syringaldehyde and disyringylmethane and their deuterium enriched analogs had the same response factors. This assumption allowed for the subtraction of the nondeuterated portion of the GC peaks; the amount of syringaldehyde and disyringylmethane in each sample was previously determined by SIMS. Thus, the GC areas of **15** and **16** were compared to the GC areas of deuterated syringaldehyde and deuterated disyringylmethane, respectively. This GC area ratio was then divided by the moles of deuterated compound contained in the sample and the volume of the sample. The mass spectra of the sulfur compounds, used in their identification, are as follows: m/e (%)

15 200 (M^+, 26.1), 167 (100.0), 148 (34.0), 136 (21.0).

16 366 (M^+, 10.8), 332 (2.1), 200 (6.1), 168 (38.0), 167 (100.0), 148 (20.5), 136 (13.3).

SYNTHESES

Anthrahydroquinone

Anthrahydroquinone was prepared in a nitrogen atmosphere by adding 150 mL of oxygen-free water, enough 30% ultrapure NaOH to make at least a 1N NaOH solution, the preweighed anthraquinone (1.2492 g, 2 molar equivalents; 0.3123 g, 0.5 molar equivalent; or 0.0625 g, 0.1 molar equivalent), and an excess (~ 3 times) of $Na_2S_2O_4$ to a 250 mL Erlenmeyer flask. The solution was stirred for at least an hour, after which 2M H_2SO_4 was added until precipitation occurred. The solid was collected by filtration, washed twice with oxygen-free water, and placed in the reaction vessel.

Syringyl Alcohol[25]

To a 250 mL Erlenmeyer flask was added 84 g of distilled water, 4.25 g of NaOH, and 10.00 g of syringaldehyde. With stirring, heat was applied until the syringaldehyde dissolved. Removal of the heat was accompanied by the addition of 1.25 g of $NaBH_4$. After an hour, an additional 1.25 g of $NaBH_4$ was added. The reaction was stirred overnight, neutralized with 5M H_2SO_4, and refrigerated. The precipitated solid was collected by filtration and recrystallized twice from chloroform/hexane: the yield of colorless crystals was 7.26 g, (72.6%); corrected m.p. 132-136°C (literature: 134°C); ^{1}H-NMR ($CDCl_3$) δ 1.64 (t, 1, J = 6 Hz, Ph-CH_2OH), 3.90 (s, 6, -OCH_3), 4.61 (d, 2, J = 6 Hz, Ph-CH_2OH), 5.50 (s, 1, Ph-OH), 6.61 (s, 2, aryl); MS m/e (%) 184 (100, M^+), 167 (33.5), 123 (39.1), 109 (46.0), 95 (33.9), 81 (41.1), 65 (18.2), 53 (31.2).

Disyringylmethane

Syringyl alcohol was added to a 1N NaOH solution in the previously described reaction vessel and heated at 135°C for six hours. The reaction

solution was then neutralized with 5M H_2SO_4 and extracted with chloroform. The chloroform was separated, dried (anhydrous Na_2SO_4), and reduced to a minimum volume. Separation of the products was accomplished by placing the chloroform solution on a silica gel column and eluting with chloroform. Disyringylmethane coeluted from the column with syringaldehyde; the aldehyde was removed from the chloroform solution by extraction with an aqueous $NaHSO_3$ solution. The chloroform (now containing only disyringylmethane) was dried (anhydrous Na_2SO_4) and evaporated. The resulting solid was recrystallized from toluene/35-60°C petroleum ether: yield = 63%; m.p. = 110.5-111.5°C; ^{1}H-NMR ($CDCl_3$) δ 3.83 (s, 16, $-CH_2-$ and $-OCH_3$), 5.42 (s, 2, -OH), 6.39 (s, 4, aryl); ^{13}C-NMR ($CDCl_3$) ppm 41.7 (t, $-CH_2-$), 56.07 (q, $-OCH_3$), 105.34 (d, C-2, C-6), 131.79 (s, C-1), 132.76 (s, C-4), 146.62 (s, C-3, C-5).

Deuterium-Enriched Syringaldehyde

The two aromatic hydrogens of syringaldehyde were exchanged for deuteriums by heating syringaldehyde in 100% D_3PO_4.[26,27] The 100% D_3PO_4 was prepared in a nitrogen atmosphere by adding 35.5 g of P_2O_5 to 100 g of stirring 85% D_3PO_4. To an oven-dried 250-mL three-necked round-bottom flask was added the 100% D_3PO_4 and 9.5 g of syringaldehyde. Nitrogen was passed through the flask as the contents were stirred in a 50°C water bath for four days. Quenching of the reaction was accomplished by adding water to the flask, pouring the reaction solution into a larger volume of water, and carefully adding solid NaOH until the pH was near 1. The solid product was filtered from the aqueous mixture, washed with water, and dried. The filtered solution was extracted with chloroform, which in turn was dried (anhydrous Na_2SO_4) and evaporated to yield additional product. Analysis of the combined product (9.0 g) by ^{1}H-NMR showed, with respect to the methoxyl protons, an exchange of the aromatic protons corresponding to 95.7% D_2.

Deuterium-Enriched Syringyl Alcohol

Deuterium-labeled syringyl alcohol was obtained by reducing deuterium-enriched syringaldehyde with borohydride as previously described. This labeled syringyl alcohol was used in preparing the SIMS standard solutions.

Deuterium-Enriched Syringol[26,27]

In a nitrogen atmosphere, 2.00 g of syringol was added to a 100 mL oven-dried, three-necked, round-bottom flask along with 30.0 g of 100% D_3PO_4. The contents were stirred in a 50°C water bath with a constant flow of nitrogen for three days. The reaction was quenched by first adding 50 mL of water and then solid NaOH until the solution was neutral. Extraction of the solution with chloroform (dried with anhydrous Na_2SO_4 and evaporated) yielded 1.60 g of solid. The deuterium enrichment process was repeated with 33.0 g of 100% D_3PO_4. This time, 1.38 g of solid was collected; analysis by GC/MS showed no 154 ion (D_0) with 156 (D_2) as the major ion.

α-α-Dideuteriosyringyl Alcohol

The ethyl ester of syringic acid was prepared by stirring for 30 min a saturated HCl gas solution of 70 mL of ethanol containing 5.00 g (0.0252 g moles) of syringic acid. The ethanol solution was then halved by distillation and poured into 300 mL of a 2% $NaHCO_3$ solution. Filtration of the bicarbonate solution provided 4.25 g of a colorless solid. Extraction of the bicarbonate solution with chloroform (dried with anhydrous Na_2SO_4 and evaporated) yielded an additional 1.17 g of product. The total yield of ester was 5.42 g (0.0238 g mole, yield = 95.0%); ^{1}H-NMR ($CDCl_3$) δ 1.39 (t, 3, J = 7 Hz, $-CH_3$), 3.93 (s, 6, $-OCH_3$), 4.36 (q, 2, J = 7 Hz, $-CH_2-$), 5.99 (s, 1, -OH), 7.32 (s, 2, aryl).

Reduction of the ethyl ester was accomplished in a nitrogen atmosphere by adding 3.00 g of $LiAlD_4$ (1.144 equivalents) to a 500 mL oven-dried, three-necked, round-bottom flask; anhydrous ether was slowly added until a volume of 50 mL was attained. Also, 10.92 g (0.0483 g mole) of the ethyl ester was dissolved in 150 mL of anhydrous ether and added to an oven-dried 250 mL pressure-equalizing funnel. The glassware was assembled and nitrogen was slowly passed through the reaction apparatus. Addition of the ethyl ester solution to the stirred $LiAlD_4$ was completed in two hours after which the ether was refluxed for three hours.

Quenching of the reaction was done by slowly adding a saturated Na_2SO_4 solution to the stirred reaction mixture. The reaction mixture was filtered and the solid (aluminum salts) was extracted with ether and filtered again. Finally, the solid was dissolved in a dilute HCl solution and extracted with ether. The combined ether solutions were dried (anhydrous Na_2SO_4) and evaporated to give a solid which when recrystallized from chloroform/hexane yielded 2.95 g (0.0160 g mole, yield = 33%) of α,α-dideuteriosyringyl alcohol. Analysis of the product by ^1H-NMR showed the disappearance of the benzylic doublet at δ 4.61.

α,α-Dideuteriodisyringylmethane

In a nitrogen atmosphere, the previously described 250-mL reactor vessel was loaded with 2.26 g (0.0121 g mole) of α,α-dideuteriosyringyl alcohol, 110.12 g of oxygen-free water, and 16.16 g of 30% ultrapure NaOH. The reaction vessel was sealed and placed in a 135°C oil bath. After six hours, the reaction solution was cooled, acidified to a pH of about 1, and extracted with chloroform.

The chloroform was dried (anhydrous Na_2SO_4) and reduced to a minimum volume. This chloroform solution was placed on a silica gel column, which was

eluted with chloroform. The first compounds eluted were syringol and 4-methylsyringol. Analysis of these compounds by GC/MS gave their molecular weights as 154 and 171, respectively. Thus, the alkaline reaction of α,α-dideuteriosyringyl alcohol yielded trideuterated 4-methylsyringol.

Disyringylmethane and syringaldehyde quickly followed. The chloroform containing these compounds was reduced in volume, extracted with a $NaHSO_3$ solution to remove the aldehyde, dried (anhydrous Na_2SO_4), and evaporated. The resulting solid was recrystallized from toluene/35-60°C petroleum ether to yield 1.33 g (0.00413 g mole, yield = 67.7%) of α,α-dideuteriodisyringylmethane. Analysis by ^{1}H-NMR showed the loss of the benzylic protons.

Bisyringyl[28]

To a 100-mL Erlenmeyer flask was added 42 mL of 95% ethanol and 0.70 g of syringil. The ethanol was heated with stirring to boiling; 1.4 g of zinc dust was added, and the heat was removed. With continuation of the stirring, 5.6 mL of concentrated HCl was added. The zinc was removed by filtration and washed with ethanol. The combined ethanol solutions were added to 250 mL of water, and the ethanol was removed under reduced pressure. Filtering the solution gave 0.32 g of solid: yield = 50%; melting point 170-173°C (literature: 176-177°C); ^{1}H-NMR ($CDCl_3$) δ 2.81 (s, 4, $-CH_2-$), 3.84 (s, 12, $-OCH_3$), 6.36 (s, 4, aryl); ^{13}C-NMR ($CDCl_3$) ppm 38.52 ($-CH_2-$), 56.32 ($-OCH_3$), 105.19 (C-2, C-6), 132.62 and 132.81 (C-1 and C-4), 146.61 (C-3, C-5); MS m/e (%) 334 (30.1, M^+), 168 (16.9), 167 (100).

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THE APPLICATION OF AN INTRAMOLECULAR CYCLIZATION REACTION AS A DETECTOR OF ELECTRON-TRANSFER TO QUINONEMETHIDES

Dean A. Smith and Donald R. Dimmel
The Institute of Paper Chemistry
Appleton, Wisconsin 54912

ABSTRACT

Evidence has been accumulated which demonstrates the ability of anthrahydroquinone and other compounds to transfer electrons to quinonemethides (QMs) in 1N NaOH at 135°C. An electron-transfer probe compound (**6**), which incorporated a hex-5-enyl group on a QM precursor, was synthesized and reacted under the above conditions in the presence of anthrahydroquinone (AHQ). A five-membered ring compound (**10**) was identified as one of the products; cyclization of the straight-chain hex-5-enyl to a five-membered ring is diagnostic of a radical intermediate.[1,2] The principal product (**8**) corresponded to a simple reduction of the benzyl carbon of the probe compound. Thus, the sequence of reactions occurring in the presence of AHQ appears to be (a) QM formation, (b) electron-transfer from AHQ^{-2} to the QM, giving a quinonemethide radical-anion ($QM^{\cdot -}$), (c) cyclization of some $QM^{\cdot -}$s to a five-membered ring, and (d) reduction of the uncyclized $QM^{\cdot -}$s and the cyclized radicals.

Glucose was also found to transfer electrons to the QMs formed from **6**. The glucose reaction provided greater yields of cyclized product and also reasonable yields of three unique tricyclo [7.3.0.$0^{2,7}$] dodecatrienes (**12**, **13**, and **14**). This increased yield of cyclized products appears to be due to the relatively slow rate in which glucose reduces the radical intermediates.

The ability of a compound to transfer electrons to QMs in aqueous alkali has implications as to how the compound affects the rate of lignin fragmentation and condensation reactions during the alkaline pulping of wood.

INTRODUCTION

Wood is composed of two basic elements, carbohydrates and lignin. The goal of the alkaline pulping of wood is to remove the lignin and retain the carbohydrates. Lignin removal is accomplished by the fragmentation of the lignin polymer into water soluble particles. To aid the delignification process, sodium sulfide and anthraquinone are used either separately or together. Anthraquinone as an additive is a rather recent discovery, and much interest has been generated in its mechanism of action.[3]

Studies investigating the beneficial effects of anthraquinone indicate that it aids pulping by oxidizing the aldehyde end groups of the carbohydrates to alkali-stable acid groups.[4] During this process, anthraquinone is reduced to anthrahydroquinone (AHQ). Anthrahydroquinone is able to fragment lignin by a reductive process which regenerates anthraquinone. Thus, the beneficial effects of anthraquinone appear to be due to a cyclic redox mechanism[4] (Fig. 1).

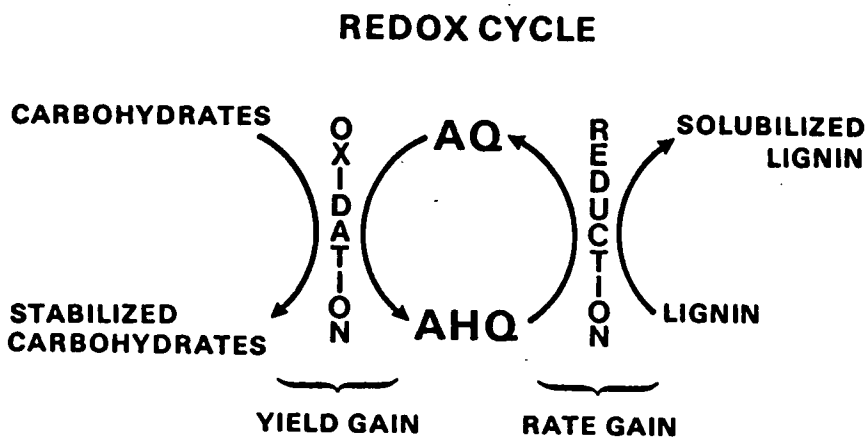


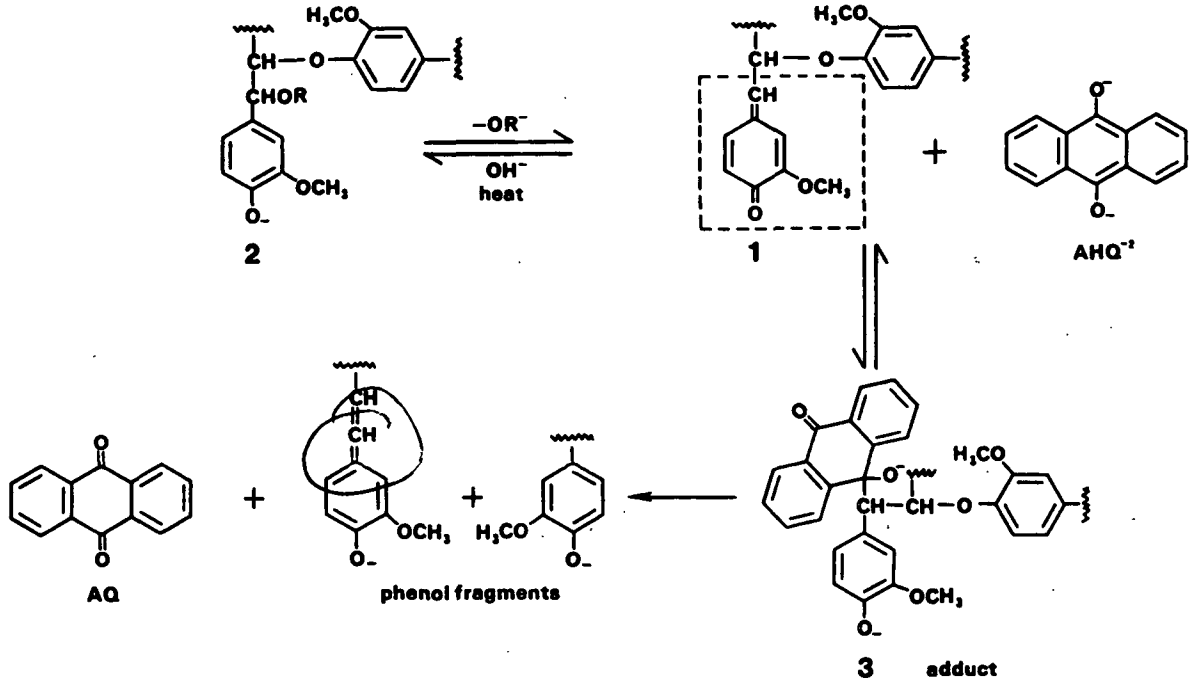
Figure 1. The cyclic redox mechanism by which anthraquinone aids wood pulping.

Fragmentation of lignin model compounds by AHQ has been extensively studied in order to understand the chemistry of AHQ. One of the proposed mechanisms[5-7] for an AHQ induced lignin fragmentation process is shown in Scheme 1. The steps in the mechanism are similar to the proposed method of lignin cleavage by sodium sulfide: addition of a nucleophile to a quinonemethide (1) and subsequent loss of a phenolate ion fragment.

The lignin structure (2) depicted in Scheme 1 contains a free phenol and a leaving group at the α-position, both essential for quinonemethide (QM) formation. Also, the structure contains the linkage most prevalent in lignin, a β-aryl ether bond.[8] Cleavage of this structure by AHQ begins when lignin is heated in base, a process which generates QMs. An AHQ^{-2} ion can then add to the α-position

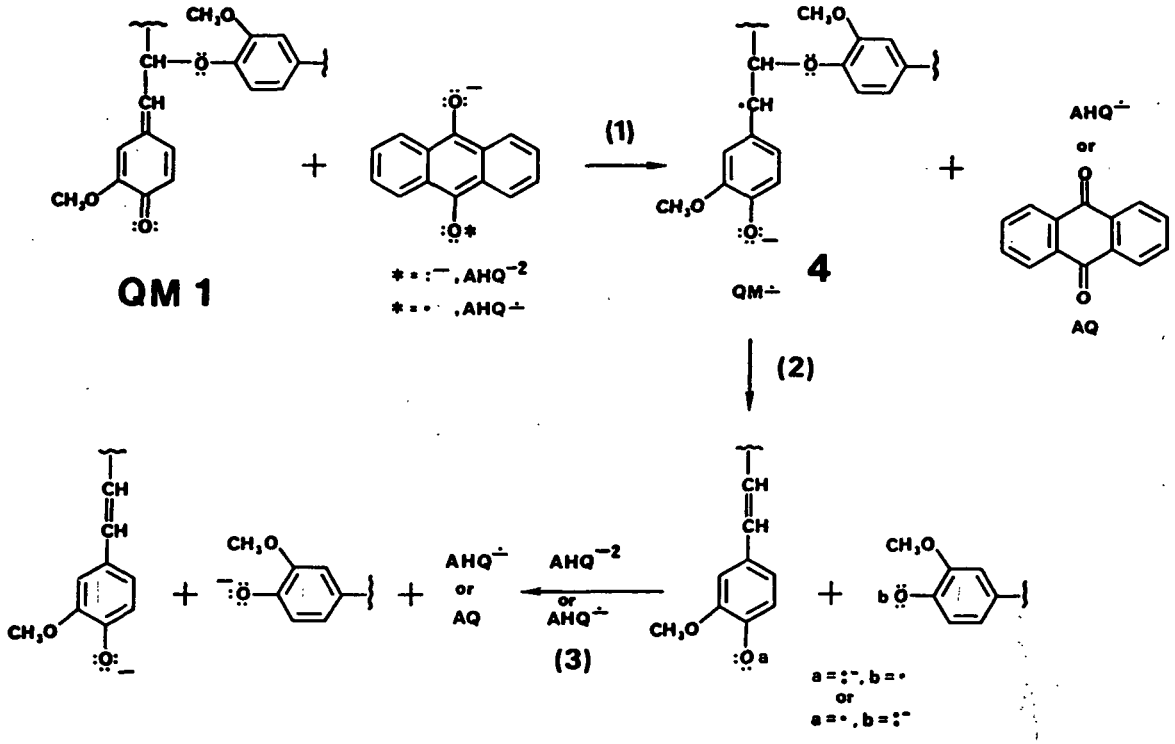
of the QM to form an "adduct" (3). The adduct is believed to break apart in a concerted cleavage of the β-aryl ether linkage, with the concurrent generation of anthraquinone. Therefore, the fragmentation of lignin by AHQ, as viewed by this ionic mechanism, involves the two electron reduction of QMs by AHQ^{-2} via a sequence of bond formation and a β-elimination at the α- and β-positions.

Scheme 1. Delignification by an AHQ adduct-ionic mechanism. Dashed square outlines a QM structure.



Recent results have indicated that AHQ is not limited to adduct formation but may also reduce QMs and eventually fragment lignin by electron transfer.[3,9-11] The requirement of electron-poor and electron-rich substrates, necessary for electron transfer, is met with a QM and AHQ, respectively. Fragmentation of lignin by electron transfer[3] (Scheme 2) is viewed as beginning with a transfer of an electron from AHQ^{-2} to a QM producing $AHQ^{\bullet-}$ and a quinonemethide radical anion (4). The quinonemethide radical anion ($QM^{\bullet-}$) then fragments to a phenolate ion and a phenoxy radical.

Scheme 2. Delignification by AHQ^{-2} electron transfer to a QM.



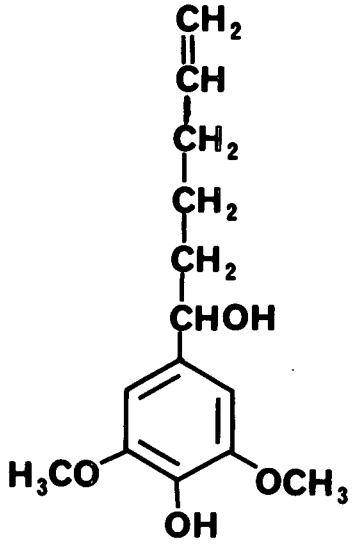
Evidence supporting an electron transfer fragmentation process was provided by a study of the cleavage of a β-aryl ether QM in solution with electrochemically generated $AHQ^{\cdot-}$.[9] Cleavage of the β-aryl ether bond was believed to be the result of electron transfer from $AHQ^{\cdot-}$ to the QM. The study, however, employed conditions quite different from pulping; the temperature was ambient and the solvents were principally organic.

In order to determine if certain reagents can transfer electrons to QMs under conditions similar to alkaline pulping (1N NaOH and 170°C), we have synthesized and studied the alkaline reactions of a compound which is soluble in alkali, can form a QM, and can show the existence of a radical intermediate. The reaction of the compound with chemicals typically present during pulping, such as AHQ, carbohydrates, and sulfide, is the subject of this report.

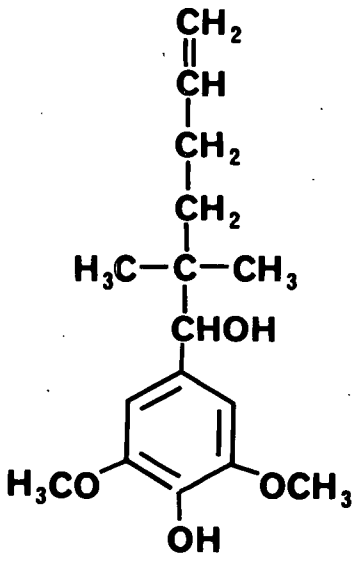
RESULTS AND DISCUSSION

Cyclization of hex-5-enyls to five-membered rings is generally assumed to be diagnostic of the intermediacy of radicals in reaction mechanisms.[1,2] A lignin model compound incorporating a hex-5-enyl (5) was prepared to determine if electron-transfer to QMs is possible under pulpinglike conditions. Model compound **5** was easily prepared by the Grignard reaction of 5-bromo-1-pentene with syringaldehyde. The model contains the substituents necessary for QM formation, a free phenol and a leaving group at the α-carbon of a para-side chain. Unfortunately, the alkaline reactions of **5** at 135°C resulted in only dehydration, yielding styrene products. Even addition of AHQ did not prevent dehydration.

To eliminate dehydration, a second model (**6**) was prepared with methyl groups at the β-position. Besides blocking dehydration, these methyl groups will have the additional benefit of increasing the rate of cyclization.[12] Synthesis of **6** was accomplished by converting 5-chloro-5-methyl-1-hexene to a Grignard reagent and mixing the latter with syringaldehyde.



5



6

NaOH Reactions

The reaction of **6** in 1N NaOH at 135°C for four hours provided only 2,6-dimethoxyphenol (syringol). Syringol was always observed as a product when **6** was reacted in hot alkali. Although the mechanism of syringol formation is not completely understood, its formation does not appear to be related to electron transfer. Fortunately, no dehydration products were formed in any significant yields; the incorporation of the methyl groups apparently prevented this undesirable reaction.

When the reaction time was increased to 18 hours, small yields of compounds **10**, **13**, and **14** were observed (Fig. 2). These products along with compounds **8** and **12** were isolated by column chromatography and identified by spectroscopic techniques.

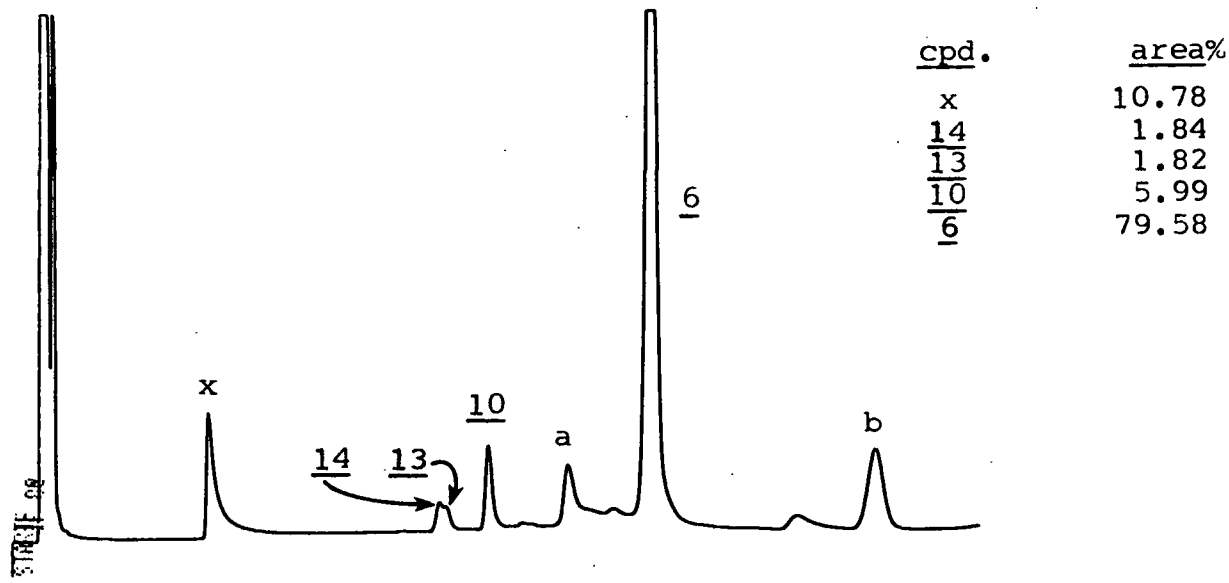


Figure 2. The GC chromatogram of the products formed when **6** was reacted in 1N NaOH at 135°C for 18 hours. x = syringol, a and b = unidentified products with molecular weights of 262 and 280, respectively.

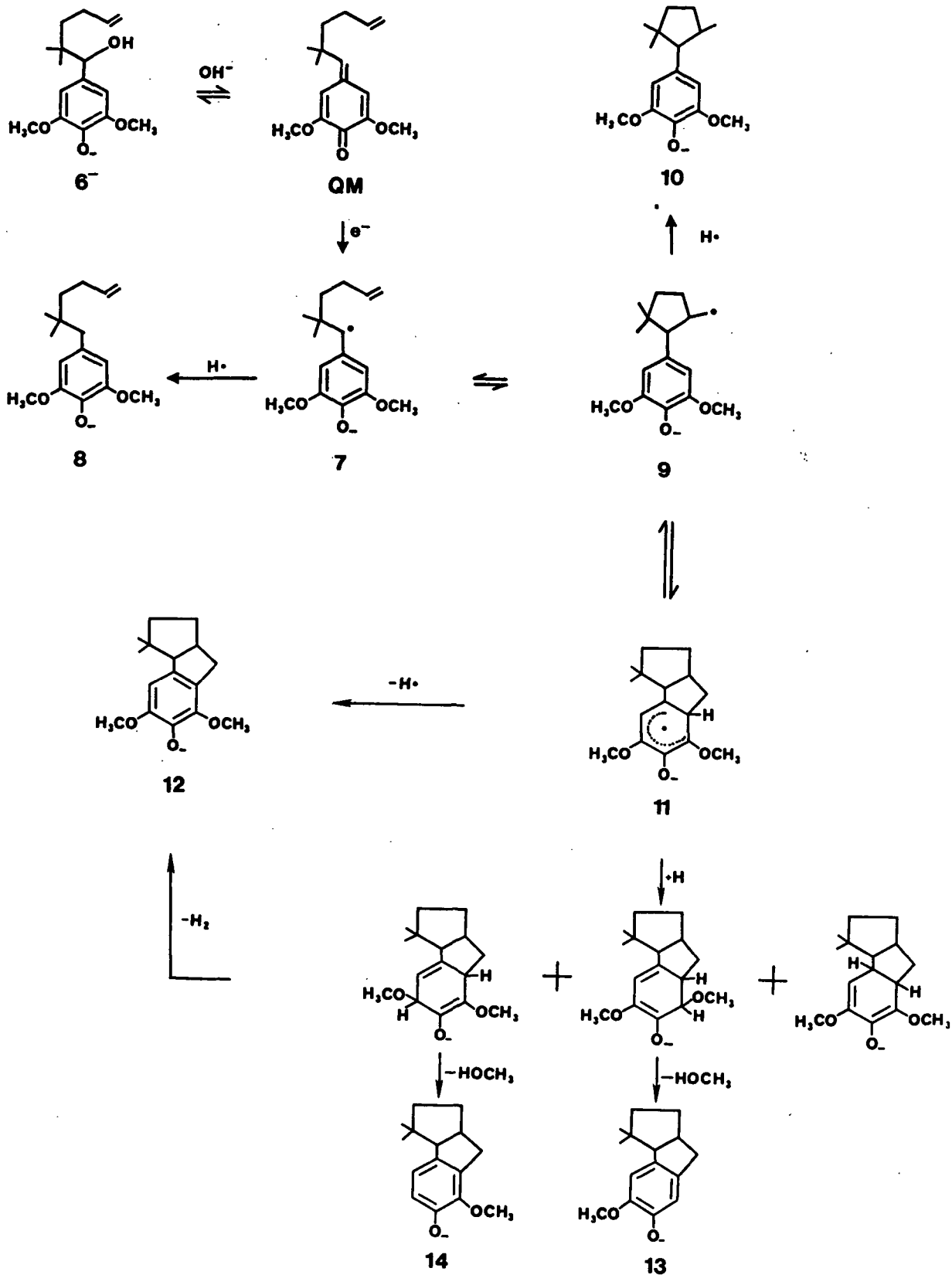
Evidence has been obtained that phenolate ions (which could be considered as an electron-rich substrate) are able to transfer electrons to QMs.[13,14] Apparently, the phenolate ions of **6** transferred electrons to QMs, forming $QM^{\cdot-}$ **7** (Scheme 3). This $QM^{\cdot-}$ can then either accept a hydrogen atom to form **8** or cyclize to radical anion **9**. Acceptance of a hydrogen atom by **9** would result in cyclized product **10**.

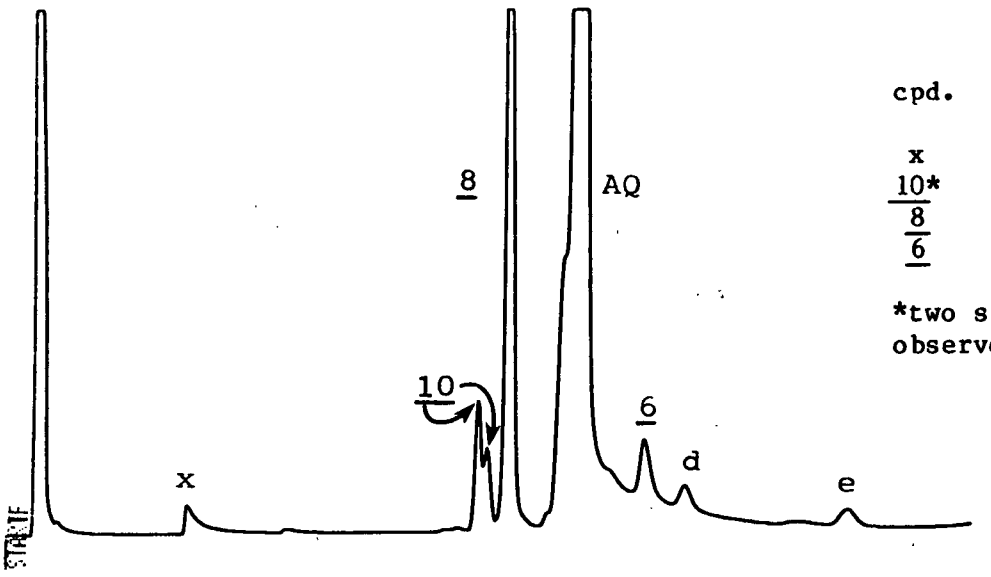
As a second alternative, the radical of **9** must also be able to attack the aromatic ring to form radical anion **11** (Scheme 3). Once **11** is generated, the loss of a hydrogen atom results in **12**. Acceptance of a hydrogen atom at the three positions occupied by the radical is another possibility for **11**. Loss of molecular hydrogen from these intermediates would again form **12**. However, two of the intermediates can also lose methanol to form **13** and **14**. Thus, the formation of the cyclized products **10**, **13**, and **14** substantiates the ability of phenolate ions to transfer electrons to QMs.

Anthrahydroquinone Reactions

When two equivalents of AHQ were present during the heating of **6** at 135°C in aqueous alkali, two products (**8** and **10**) were observed in good yields in less than two hours (Fig. 3). This result demonstrates two aspects of AHQ: (a) the ability of AHQ^{-2} to transfer electrons to QMs and (b) the good rate of hydrogen atom transfer to radical intermediates by AHQ^{-2}. The first is easily understood, since a short reaction time yielded large quantities of products. An explanation of the second is provided by **8** being the major product. Evidently, AHQ^{-2} supplies hydrogen atoms to $QM^{\cdot-}$ **7**, forming **8**, faster than $QM^{\cdot-}$ **7** cyclized to **9**. Even though it was not the major product, the formation of **10**, the cyclized product, demonstrates the ability of AHQ^{-2} to transfer electrons to QMs.

Scheme 3. Formation of products **8**, **10**, **12**, **13**, and **14** by electron transfer.





cpd.	area%
x	6.62
10*	9.73
8	76.10
6	7.55

*two stereoisomers observed

Figure 3. The GC chromatogram of the products formed when **6** was reacted with 2 molar equivalents of AHQ in 1N NaOH at 135°C for 2 hours. x = syringol, d and e = unidentified products with molecular weights of 280.

Carbohydrate Reactions

Fullerton and Wilkins have shown that the fragmentation of β-aryl ether lignin models is promoted by "reducing sugars."[15] Quinonemethide-carbohydrate adducts were synthesized and found to fragment a β-aryl ether linkage under pulpinglike conditions; an ionic mechanism of fragmentation via an adduct intermediate was proposed. Yet, as in AHQ induced model fragmentation, the adduct may not be part of the reaction sequence which leads to cleavage.

Can carbohydrates transfer electrons to quinonemethides? As shown in Fig. 4, the addition of five molar equivalents of glucose to an alkaline reaction of **6** provided **10** as the major product. Also formed were **8**, **12**, **13**, and **14**. As compared to AHQ addition, the yield of **8** was greatly decreased, while the yield of **10** was vastly increased. Evidently, glucose is a poor supplier of hydrogen

atoms, allowing **7** to cyclize and form good yields of **10**. The formation of this product, along with **12**, **13**, and **14**, demonstrates the ability of glucose to transfer electrons to QMs.

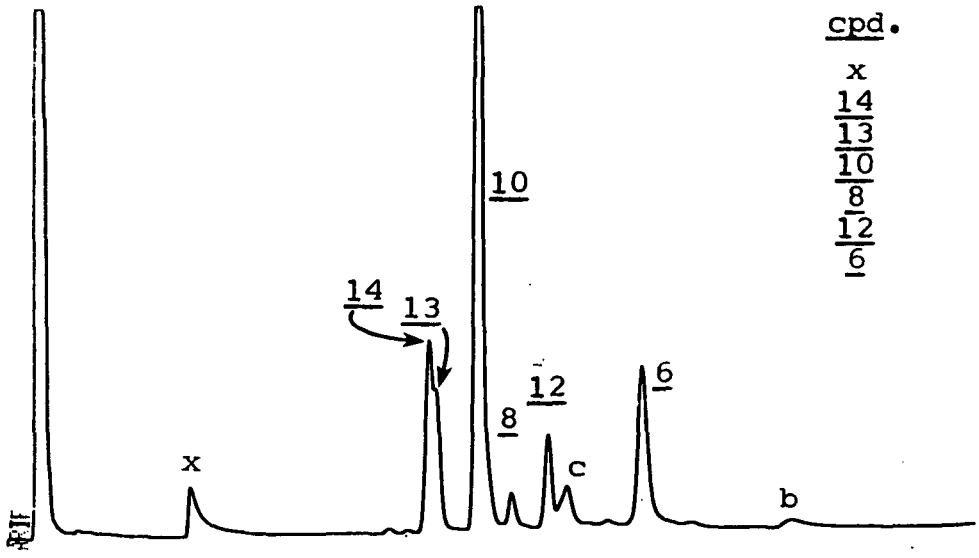


Figure 4. The GC chromatogram of the products formed when **6** was reacted with 5 molar equivalents of glucose in 1N NaOH at 135°C for 18 hours. x = syringol, b and c = unidentified products with molecular weights of 280 and 264, respectively.

A further study involved a determination of the necessity of the carbohydrate free aldehyde for electron transfer. This necessity was determined by adding methyl-α- and methyl-β-D-glucoside to separate reactions of **6**. These derivatives lock glucose into the six-membered ring and thus prevent mutarotation (the interconversion of glucose from the six-membered ring to the straight-chain free aldehyde). When compared to glucose, both derivatives gave less cyclized product (Fig. 5). Of the two glucose derivatives, the β one provided better yields of reduction products. Past research has shown that the β

derivative degrades faster in alkali to the free aldehyde than the α derivative.[16] Apparently, the free aldehyde is necessary for good electron transfer.

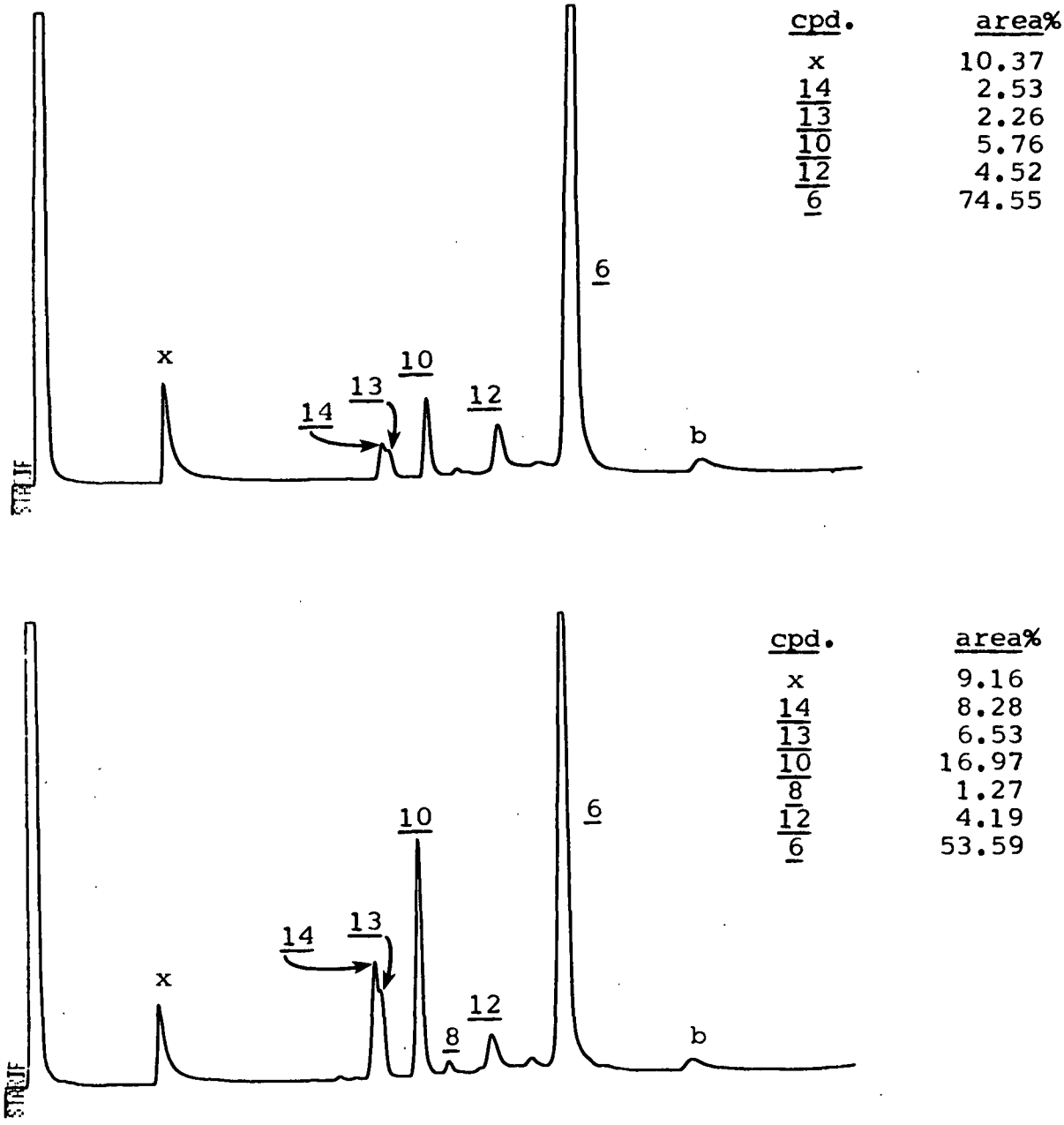


Figure 5. A comparison of the amounts of products formed when **6** was reacted with α- (top) and β- (bottom) methylglucose in 1N NaOH at 135°C for 18 hours. For x and b, see Fig. 4.

Other Pulping Reagents

Two compounds used to aid delignification, sodium sulfide and sodium sulfite, were also tested for their ability to transfer electrons to the QMs of **6**. However, these inorganics did not provide any increase in cyclized products as compared to the reaction of **6** with no additives. Sulfide was even reacted at 170°C and still found to be unable to transfer electrons. The inability of sulfide to transfer electrons is in agreement with past research[17] and our other studies.[14]

CONCLUSIONS

The cyclization of **6** to a five-membered ring product(s) provides conclusive evidence for the transfer of electrons from phenolate ions, AHQ, and glucose to the QMs formed from **6** in 1N NaOH at 135°C. The ability of these compounds to transfer electrons to QMs in aqueous alkali has implications as to the mechanism by which they can affect the rates of lignin fragmentation and condensation reactions during the alkaline pulping of wood.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer Model 700 infrared spectrometer and standardized with polystyrene. A Jeol FX 100 spectrometer was used to obtain the NMR spectra. The mass spectra were obtained with a Hewlett Packard Model 5985 GC-MS spectrometer using a six foot 3% silicone OV-17 on 100/120 chromosorb W-HP MAOT-350 column.

Syringaldehyde and 4-bromo-1-butene were obtained from Aldrich Chemical Co., Milwaukee, Wisconsin, while 1-bromo-4-pentene was obtained from ICN Pharmaceuticals, Inc., K & K Laboratories, Plainview, New York. Ultrapure NaOH

was obtained as a 30% solution from Alfa Products, Danvers, Massachusetts. Silica gel 60 (70-230 mesh ASTM) was used in all chromatographic separations.

Oxygen-free water was prepared by boiling distilled water for about 30 minutes, after which nitrogen was dispersed into the water as it cooled to room temperature. After cooling, the water was sealed until needed.

SYNTHESES

6-Hydroxy-6-(3',5'-dimethoxy-4'-hydroxyphenyl)-1-hexene (5)

To an oven-dried 500 mL three-necked round-bottom flask flushed with nitrogen, was added 0.90 g (0.037 g atom) of magnesium turnings and enough anhydrous ether to cover the turnings. Connected to the flask was an oven-dried 250-mL pressure equalizing addition funnel containing a 150 mL anhydrous ether solution of 5.5 g (0.037 g mole) of 5-bromo-1-pentene. A constant flow of nitrogen was maintained through the apparatus as a few drops of 1,2-dibromoethane and about 10 mL of the ether solution were used to initiate the reaction. The remaining ether solution was added to the stirred contents of the flask at a rate that gently refluxed the ether. After the complete addition of the ether, the solution was refluxed for 90 min in a 40°C water bath. Then about 75 mL of freshly distilled tetrahydrofuran (THF) were added, and the water bath temperature was increased to 70°C. Syringaldehyde (2.80 g, 0.015 mole) dissolved in 40 mL of THF was dripped into the reaction vessel. An hour after the syringaldehyde addition was complete, the reaction was quenched with 5 mL of water followed by 2M H_2SO_4. The THF was separated, filtered, dried (anhydrous $MgSO_4$), and evaporated to give a yellow liquid. Analysis of the liquid by ^{1}H-NMR and GC/MS identified the product as the ketone of the title compound.

The ketone was reduced by dissolving the yellow liquid in 50 mL of ethanol and adding dropwise 50 mL of distilled water containing 1.5 g of $NaBH_4$. After stirring overnight, the reaction solution was filtered, quenched with 100 mL of saturated ammonium chloride, and neutralized with 0.5M H_2SO_4. The aqueous solution was extracted twice with 70 mL of chloroform. The chloroform was combined, dried (anhydrous Na_2SO_4), and evaporated to give a greenish solid. This solid was recrystallized from toluene/35-60°C petroleum ether to yield 1.70 g of a colorless solid: m.p. 91-92°C; IR (mull) cm^{-1} 3150-3600 (Ph-OH and HCOH), 1615 (CH_2=CH-); ^{1}H-NMR ($CDCl_3$) δ 1.5 (m, 2, C4-H_2), 1.7 (m, 2, C3-H_2), 2.0 (m, 2, C5-H_2), 2.08 (s, 1, -CHOH-, exchangable with D_2O), 3.87 (s, 6, -OCH_3), 4.6 (m, 1, -CHOH-), 4.9-5.1 (m, 2, CH_2=), 5.56 (s, 1, Ph-OH, exchangable with D_2O), 5.56-6.01 (d of d of t, 1, J = 17, 10, and 6 Hz, =CH-), 6.55 (s, 2, aryl); ^{13}C-NMR ($CDCl_3$) ppm 25.1 (t, C4), 33.5 (t, C5), 38.4 (t, C3), 56.1 (q, -OCH_3), 74.4 (d, C6), 102.4 (t, CH_2=), 114.3 (d, C2', C6'), 133.6 (s, C1'), 135.8 (s, C4'), 138.3 (d, =CH-), 146.6 (s, C3', C5'); MS m/e (%) 252 (41, M+), 183 (100), 155 (47), 140 (30), 123 (95), 95 (57), 77 (32), 41 (53).

5-Hydroxy-5-methyl-1-hexene

To an oven-dried 500 mL three-necked round bottom flask was added 9.50 g (0.391 g atom) of magnesium turnings and approximately 75 mL of anhydrous ether. Connected to the flask was an oven-dried 250 mL pressure equalizing addition funnel containing 50.0 g (0.365 g mole) of 4-bromo-1-butene and 200 mL of anhydrous ether. In order to initiate the reaction, about 0.5 mL of 1,2-dibromoethane was added in conjunction with approximately 10 mL of the 4-bromo-1-butene solution. The remaining 4-bromo-1-butene solution was added in a manner that maintained the gentle reflux of the ether. A half hour after the last addition of 4-bromo-1-butene, 50 g (0.962 g mole) of acetone was slowly

added. Two hours after the complete addition of the acetone, the reaction was quenched first with water and then with 5M HCl until the aqueous phase was clear. The ether was separated, dried (anhydrous Na_2SO_4), and evaporated. The title compound was distilled at 54-55°C/14 mm Hg as a colorless liquid: yield = 60.1%; IR cm^{-1} 3150-3700 (OH) and 1640 ($-CH=CH_2$); ^1H-NMR ($CDCl_3$) δ 1.22 (s, 6, $-CH_3$), 1.54 (t, 2, J = 6, C4-H_2), 1.76 (s, 1, -OH), 2.0-2.3 (m, 2, C3-H_2), 4.9-5.1 (m, 2, $CH_2=$), 5.65-6.09 (d of d of t, 1, J = 17, 10, and 6 Hz, =CH-); ^{13}C-NMR ($CDCl_3$) ppm 28.7 (t, C4), 29.2 (q, $-CH_3$), 42.7 (t, C3), 70.7 (s, C5), 114.1 (t, $CH_2=$), 138.7 (d, =CH-).

5-Chloro-5-methyl-1-hexene[18]

To prepare the title compound, 5-hydroxy-5-methyl-1-hexene was shaken with concentrated hydrochloric acid at room temperature for 5 min. The organic liquid was separated, dried (anhydrous Na_2SO_4), and distilled at 93-96°C/252 mm Hg to give a clear liquid: yield = 68%; IR cm^{-1} 1640 ($-CH=CH_2$); ^1H-NMR ($CDCl_3$) δ 1.58 (s, 6, $-CH_3$), 1.7-1.9 (m, 2, C4-H_2), 2.1-2.4 (m, 2, C3-H_2), 4.9-5.2 (m, 2, $CH_2=$), 5.63-5.97 (d of d of t, 1, J = 17, 10 Hz, and 6, =CH-); ^{13}C-NMR ($CDCl_3$) ppm 29.5 (t, C4), 30.1 (q, $-CH_3$), 32.4 (t, C3), 45.0 (s, C5), 114.5 (t, $CH_2=$), 137.6 (d, =CH-).

Silated Syringaldehyde

Silated syringaldehyde was prepared by the method of Moreau et al.,[19] with the reaction done in dichloromethane at 39°C. Unreacted syringaldehyde was removed by extracting the dichloromethane solution with 1N NaOH. The dichloromethane was subsequently washed with water, dried (anhydrous Na_2SO_4), and removed, leaving a yellowish solid. Recrystallization of the solid from toluene/50-110°C petroleum ether at 0°C gave a 79% yield of colorless needles; m.p. 80.5-82°C; IR cm^{-1} 1680 (CHO); ^1H-NMR ($CDCl_3$) δ 0.25 (s, 9, $-SIMe_3$), 3.88 (s, 6, $-OCH_3$), 7.11 (s, 2, aryl), 9.82 (s, 1, -CHO); ^{13}C-NMR ($CDCl_3$) ppm 0.10 (q, $-SIMe_3$), 55.4 (q,

$-OCH_3$), 106.1 (d, C2, C6), 128.8 (s, C4), 151.15 (s, C3, C5), 190.00 (d, -CHO), Cl was not observed; MS m/e (%) 254 (28, M+), 239 (45), 225 (16), 224 (100), 223 (34), 73 (24).

5,5-Dimethyl-6-hydroxy-6-(3',5'-dimethoxy-4'-hydroxyphenyl)-1-hexene (6)

Preparation of the Grignard reagent of 5-chloro-5-methyl-1-hexene proved to be rather difficult; refluxing ether resulted in the formation of undesired products. These undesired products were prevented by using large volumes of ether at room temperature. However, these conditions prevented the initiation and continuation of the Grignard reaction. To facilitate the reaction, periodic additions of methyl iodide were used to first initiate and then help maintain the reaction. Thus, by-products from methylmagnesium iodide were formed which had to be subsequently removed.

While in a nitrogen atmosphere, 1.0 g (0.0411 g atom) of magnesium turnings and 150-mL of anhydrous ether were added to an oven-dried 500-mL three-necked round-bottom flask. Added to two oven-dried 250-mL pressure equalizing addition funnels were 50-mL of anhydrous ether with 1.5 g (0.0113 mole) of 5-chloro-5-methyl-1-hexene and 240 mL of anhydrous ether with 2.0 g (0.0141 mole) of methyl iodide, respectively. The glassware was assembled and approximately a fourth of the methyl iodide solution was added to the stirred turnings. When the reaction had started, the dropwise addition of the 5-chloro-5-methyl-1-hexene solution was begun. This addition spanned 8-10 hours during which the methyl iodide solution was periodically added.

After the reaction solution had stirred overnight, silated syringaldehyde dissolved in anhydrous ether was added dropwise until the brown color associated with the addition was no longer observed. The reaction was quenched with water

followed by a small amount of 2M H_2SO_4. The entire solution was filtered (to remove unreacted Mg) and additional 2M H_2SO_4 was added. The acid (approximately 1N) and ether layers were allowed to sit together overnight to remove the silyl protecting group.

The ether layer was separated and extracted with a NaOH solution (1-2N) to remove the phenolic products. This extraction often resulted in a precipitate which was assumed to be the sodium salt of the desired product. Any precipitated solid was collected by filtration and redissolved in ether with the help of mild sulfuric acid (approximately 0.25M). The ether from the alkali extraction contained desired product and the liquid by-products. This ether was separated and extracted with mild acid.

The hydroxide solution contained the phenolic by-products and some desired product. This solution was slowly acidified with frequent extractions with ether. The ether was separated, extracted with mild acid, and analyzed by GC. As soon as material other than desired product was extracted by the ether, the hydroxide solution was discarded. Ether solutions containing desired product (which included the original hydroxide extracted ether, the ether containing the precipitate, and the ether extracts of the hydroxide solution) were combined, dried (anhydrous Na_2SO_4), and evaporated. The resulting solid was recrystallized from hot toluene to give an off-white solid (**6**): m.p. 111-112.5°C; IR (mull) cm^{-1} 3150-3600 (OH's) and 1610 (CH_2=CH-); ^{1}H-NMR ($CDCl_3$) δ 0.86 and 0.93 (two s, 3 + 3, gem-dimethyls), 1.4 (m, 2, C4-H_2), 1.63 (broad s, 1, -CHO<u>H</u>-), 2.0 (m, 2, C3-H_2), 3.87 (s, 6, -OCH_3), 4.39 (s, 1, -C<u>H</u>OH-), 4.8-5.1 (m, 2, CH_2=), 5.46 (s, 1, Ph-OH), 5.63-5.96 (d of d of t, 1, J = 17, 10, and 6 Hz, =CH-), 6.54 (s, 2, aryl); shaking the NMR solution with two drops of D_2O removed the hydroxyl proton signals; ^{13}C-NMR ($CDCl_3$) ppm 22.9 and 23.0 (two q, gem-dimethyls), 28.4 (d,

C4), 38.0 (d, C3), 56.2 (q, $-OCH_3$), 81.0 (d, -CHOH-), 104.5 (d, C2', C6'), 113.6 (t, CH_2=), 132.9 (s, C4'), 133.6 (s, C1'), 139.2 (d, =CH-), 146.0 (s, C3', C5'); MS m/e (%) 280 (7.1, M+), 183 (100.0), 155 (19.2), 140 (11.8), 123 (32.9), 95 (16.6), 55 (14.9).

ALKALINE REACTIONS OF **6**

All reaction solutions of **6** were prepared in a nitrogen atmosphere with oxygen-free water and 30% ultrapure NaOH. The reactions were conducted in stainless steel pressure vessels (bombs) of 4 mL capacity. Water and NaOH solution were added to make a 3.5 mL, 1N NaOH solution. The amount of **6** in each bomb was 0.0196 g (0.020 mole/liter).

The additives used were as follows: AHQ, as an AHQ-diacetate derivative,[20] (0.0412 g, 2 molar equivalents), glucose (0.0631 g, 5 molar equivalents), α- and β-methyl-D-glucose (0.0680 g, 5 molar equivalents), Na_2S (0.0109 g, 2 molar equivalents), and Na_2SO_3 (0.0441 g, 5 molar equivalents). The bombs were sealed and tumbled in a 135°C oil bath for times ranging from 2 to 18 hours. After the desired length of time, the bombs were cooled in water. The contents of the bombs were neutralized with 2M H_2SO_4 and extracted with chloroform. Analysis of the chloroform solutions was by GC/MS.

ISOLATION AND CHARACTERIZATION OF PRODUCTS

Isolation Procedures

Products **10**, **12**, **13**, and **14** were obtained from the reaction of **6** with 5 molar equivalents of glucose at 135°C in the previously described bombs. This procedure was repeated until 3.3 g of **6** were reacted. The contents of all the bombs were combined, neutralized with 5M H_2SO_4, and extracted with chloroform.

The chloroform was dried (anhydrous Na_2SO_4) and evaporated. The solid was dissolved in a minimum amount of toluene, placed on a silica gel column, and eluted with toluene, with increasing amounts of ethyl acetate added to the toluene. Products **13** and **14** were separated, while products **10** and **12** were eluted together. Solutions containing **10** and **12** were evaporated and the resulting liquid was placed on another silica gel column. Elution with petroleum ether (35-60°C) provided satisfactory separation.

Product **8** was obtained from the reaction of 0.8 g of **6** with 2 equivalents (1.2 g) of AHQ (prepared by the reduction of anthraquinone with $Na_2S_2O_4$) using a large reaction vessel (described in detail elsewhere[21]) and a temperature of 135°C. The final reaction solution was neutralized with 5M H_2SO_4 and extracted with toluene. The toluene was dried (anhydrous Na_2SO_4) and evaporated. The solid was extracted with 35-60°C petroleum ether (done to remove the anthraquinone), which in turn was evaporated to a minimum volume, placed on a silica gel column, and eluted with 35-60°C petroleum ether. A good separation of **8** was obtained. Spectral data for products **8**, **10**, **12**, **13**, and **14** are presented below and in Table 1.

5,5-Dimethyl-6-(3',5'-dimethoxy-4'-hydroxyphenyl)-1-hexene (**8**)

IR cm^{-1} 1610 ($-CH=CH_2$); ^{1}H-NMR ($CDCl_3$) δ 0.87 (s, 6, $-CH_3$), 1.2-1.4 (m, 2, C4-H_2), 2.0-2.2 (m, 2, C3-H_2), 2.42 (s, 2, C6-H_2), 3.82 (s, 6, $-OCH_3$), 4.7-5.1 (m, 2, $CH_2=$), 5.48 (broad s, 1, -OH), 5.50-6.02 (d of d of t, 1, J = 17, 10, and 6 Hz, =CH-), 6.31 (s, 2, aryl); MS m/e (%) 264 (19.8, M+), 168 (40.6), 167 (100.0).

Table 1. The ^{13}C-NMR data for the products formed from the reaction of **6** in 1N NaOH at 135°C.

Product	**8**	**10**	**12**	**13**	**14**
Carbon					
C_1	48.3 (t)	64.8 (d)	61.5 (d)	61.5 (d)	59.7 (d)
C_2	34.1 (s)	42.4 (s)	44.8 (s)	—[a]	—[a]
C_3	28.7 (t)	40.5 (t)	38.1 (t)	40.9 (t)	38.5 (t)
C_4	40.8 (t)	31.0 (t)	32.2 (t)	32.3 (t)	32.2 (t)
C_5	139.2 (d)	37.4 (d)	43.6 (d)	43.8 (d)	43.9 (d)
C_6	113.6 (t)	19.6 (q)	42.6 (t)	42.6 (t)	42.5 (t)
gem-di-Me	26.9 (q)	24.5 (q) & 29.4 (q)	24.9 (q) & 30.1 (q)	25.2 (q) & 30.2 (q)	24.9 (q) & 29.9 (q)
C_1'	133.7 (s)	133.0 (s)	136.4 (s)	127.1 (s)	134.5 (s)
C_2'	107.2 (d)	105.9 (d)	128.0 (s)	144.5 (s)	137.8 (s)
C_3'	146.1 (s)	146.3 (s)	146.3 (s)	109.9 (d)	142.2 (s)
C_4'	132.8 (s)	131.6 (s)	135.5 (s)	145.0 (s)	146.4 (s)
C_5'	146.1 (s)	146.3 (s)	142.4 (s)	135.6 (s)	113.2 (d)
C_6'	107.2 (d)	105.9 (d)	103.6 (d)	107.8 (d)	120.5 (d)
OCH_3	56.2[b] (q)	56.2[b] (q)	56.4 (q) & 59.7 (q)	56.3 (q)	60.6 (q)

[a]Not observed.
[b]Represents two methoxyls (strong peak).

2-(3',5'-Dimethoxy-4'-hydroxyphenyl)-1,1,3-trimethyl-cyclopentane (**10**)

^1H-NMR ($CDCl_3$) δ 0.66 and 0.97 (two s, 3 + 3, gem-dimethyls), 0.93 (d, 3, J = 6 Hz, $-CH_3$), 0.8-2.3 (several m, C1-H, C3-H_2, C4-H_2, C5-H_2), 3.87 (s, 3, $-OCH_3$), 5.39 (s, 1, -OH), 6.35 (s, 2, aryl); MS m/e (%) 264 (81.4, M+), 168 (100.0), 167 (43.1).

12,12-Dimethyl-4,6-dimethoxy-5-hydroxy-tricyclo [7.3.0.$0^{2,7}$] 2,4,6-dodecatriene (**12**)

^1H-NMR ($CDCl_3$) δ 0.70 and 1.15 (two s, 3 + 3, gem-dimethyls), 0.8-3.2 (several m, C1-H, C3-H_2, C4-H_2, C5-H_2), 3.84 and 3.86 (two s, 3 + 3, $-OCH_3$), 5.58 (s, 1, -OH), 6.47 (s, 1, aryl); MS m/e (%) 262 (100.0, M+), 206 (20.2), 205 (78.8).

12,12-Dimethyl-5-hydroxy-4-methoxy-tricyclo [7.3.0.$0^{2,7}$] 2,4,6-dodecatriene (13)

^{1}H-NMR ($CDCl_3$) δ 0.72 and 1.16 (two s, 3 + 3, gem-dimethyls), 0.9-3.2 (several m, C1-H, C3-H_2, C4-H_2, C5-H_2), 3.85 (s, 3, -OCH_3), 5.50 (s, 1, -OH), 6.66 and 6.68 (two s, 2, aryl); MS m/e (%) 232 (85.7, M+), 176 (27.0), 175 (100.0), 162 (12.6), 161 (10.3), 147 (12.6).

12,12-Dimethyl-5-hydroxy-6-methoxyl-tricyclo [7.3.0.$0^{2,7}$] 2,4,6-dodecatriene (14)

^{1}H-NMR ($CDCl_3$) δ 0.70 and 1.14 (two s, 3 + 3, gem-dimethyls), 0.9-3.3 (several m, C1-H, C3-H_2, C4-H_2, C5-H_2), 3.85 (s, 3, -OCH_3), 5.50 (s, 1, -OH), 6.76 (s, 2, aryl); MS m/e (%) 232 (100.0, M+), 176 (30.2), 175 (91.7), 162 (14.3), 131 (11.7), 115 (13.8).

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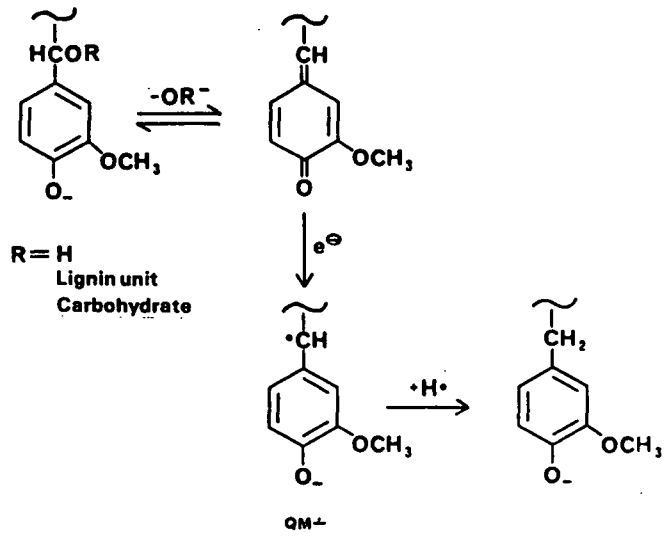
THESIS CONCLUSIONS

Three conclusions can be made from the results of the thesis. The first and most important is that **AHQ and glucose are able to transfer electrons to QMs under the conditions of pulping.** The ability of these compounds to electron transfer has significance not only in how they can interfere with condensation reactions, but also in the mechanism by which they fragment lignin.

The last two conclusions are more hypotheses, abstracting the results of the model compounds and applying them to what may occur with lignin during pulping. The first of these is that **by transferring electrons to QMs, AHQ and glucose appear capable of preventing condensation reactions.** Prevention of condensation by electron-transfer is envisioned as beginning with the transfer of an electron to a QM, producing a $QM^{\bullet-}$ (Scheme 1). This $QM^{\bullet-}$ then accepts a

Scheme 1. Lignin condensation prevention by electron-transfer.

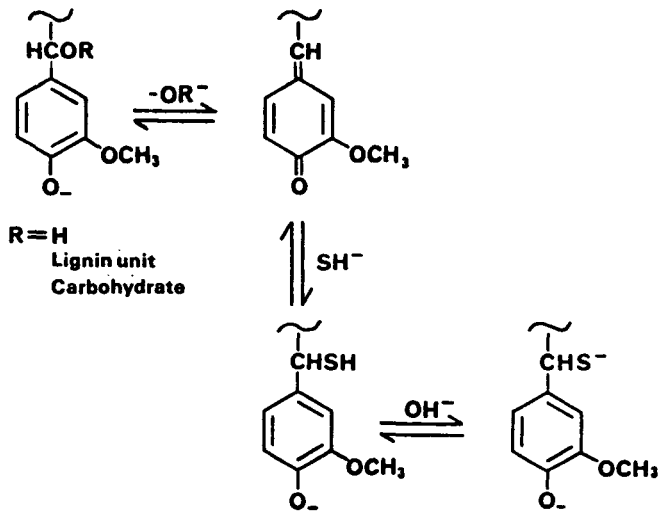


hydrogen atom to form the reduced version of the initial substrate; a QM can no longer be directly formed from this reduced substrate. Thus, electron transfer has converted a substrate capable of producing reactive QMs to a

substrate no longer capable of directly forming a QM. Consequently, electron transfer has prevented condensation.

The last conclusion is that **hydrosulfide reversibly reacts with QMs by an ionic mechanism to inhibit condensation.** The ability of sulfide to deter condensation has long been hypothesized.[1,2] However, a complete mechanism of condensation inhibition by sulfide has not been detailed. This mechanism is now envisioned as beginning with the addition of hydrosulfide to a QM to form a benzylthiol compound (Scheme 2). Under the alkalinities of pulping, the benzylthiol is easily ionized to the dianion structure. Presumably, this dianion is less able to form a QM, since S^{-2} would be a poorer leaving group as compared to OH-. But, since the steps in the mechanism are all reversible, the QM can eventually be reformed. Thus, hydrosulfide can inhibit (but not prevent as is the case with electron transfer) condensation by a reversible ionic mechanism, forming transiently stable QM-SH adducts.

Scheme 2. Lignin condensation inhibition by hydrosulfide.



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APPENDIX I

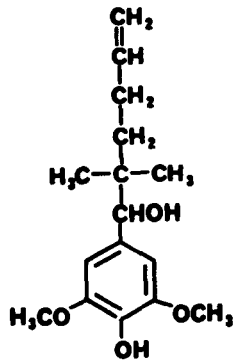
FURTHER ELECTRON-TRANSFER STUDIES

RESULTS AND DISCUSSION

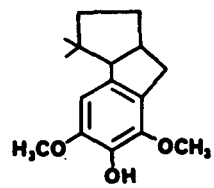
A number of more "exotic" compounds were tested for their ability to transfer electrons to the quinonemethides (QMs) formed from **1** when **1** was heated in 1N NaOH to 135°C. These compounds included three inorganics: sodium carbonate, sodium nitrate, and sodium dithionite. Only dithionite was found to produce a greater yield of cyclized products as compared to when **1** was reacted in alkali with no additives. Thus, only dithionite appears to be able to transfer electrons to QMs.

Resorcinol, ethylene diamine, and dimethyl sulfoxide (DMSO) were also added to alkaline reactions of **1**. Resorcinol and ethylene diamine appear not to have interacted with **1** at all; no increase was observed in the yields of the cyclized products as compared to when **1** was reacted alone.

In a previous study, DMSO was found to increase the rate of fragmentation of a β-aryl ether lignin model compound;[1] the increased rate could have been due to an electron-transfer mechanism. When DMSO was present during an alkaline reaction of **1**, cyclized product **2** was observed, providing evidence for the

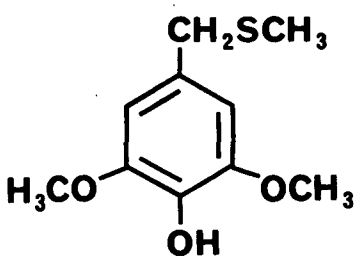


1



2

ability of DMSO to transfer electrons to QMs. However, three additional products, **3**, **4**, and **5** (identified by gas chromatography/mass spectroscopy), were produced along with other unidentified products. Apparently, dimsyl anions were formed under the reaction conditions,[1] attacked the QMs formed from **1**, and eventually led to **4**. Also, the reaction conditions can generate methyl mercaptan from DMSO.[1] Apparently, methyl mercaptan led to the formation of **3** and **5**. For unknown reasons, **5** was observed in all cases, while **3** and **4** were not. Thus, the alkaline reaction of **1** with DMSO did not determine whether the increased rate of fragmentation of the β-aryl ether model was due to either an ionic or an electron-transfer mechanism.



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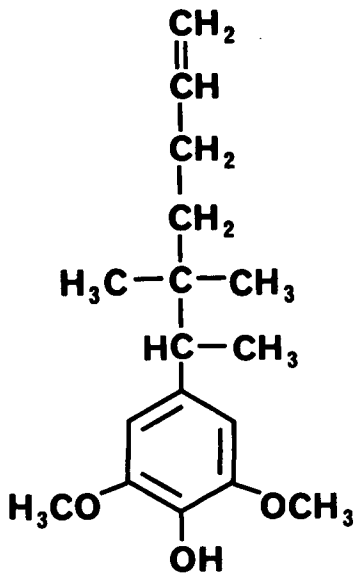

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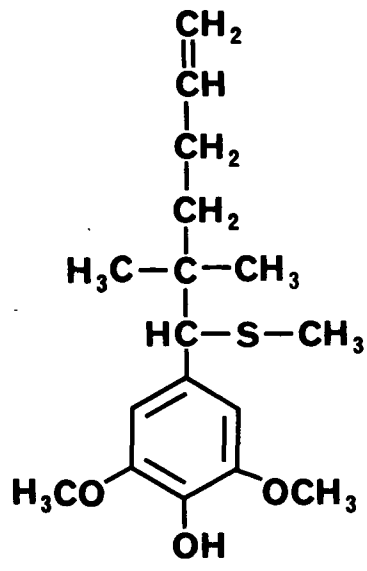

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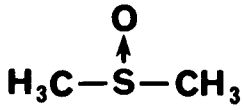
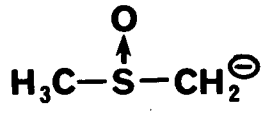
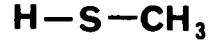


DMSO

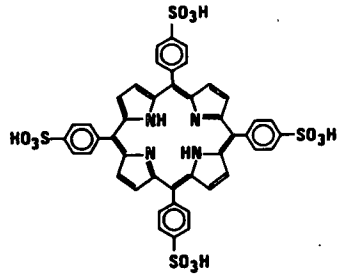


dimsyl anion



methyl mercaptan

Finally, some organometallics were reacted with **1**. Fullerton and Wright have shown that these compounds increased the rate of fragmentation of a β-aryl ether lignin model;[2] an ionic mechanism of fragmentation was proposed. However, an electron-transfer mechanism could be responsible for the observed result.



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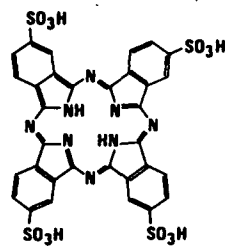

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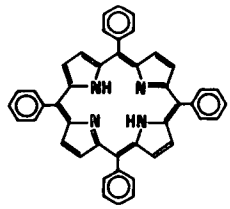

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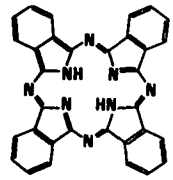


10

(Co^{III}) Tetrasulfonated Phenylporhyrin (**7**),
(Co^{III}) Tetrasulfonated Phthalocyanine (**8**),
(Co^{II}) Phenylporhyrin (**9**), and (Co^{II}) Phthalocyanine (**10**).

When Co^{III}(TsPc) (**7**) and Co^{III}(TSPP) (**8**) were added in two molar equivalents to an eighteen-hour reaction of **1**, many new products were produced (Fig. 1). In addition to these new products, there were small amounts of some of the previously identified cyclized products. Perhaps these additives formed electron-transfer products and, due to the length of the reaction, gave rise to secondary products. Further studies were prohibited due to the lack of additional organometallics.

Two other organometallics, Co^{II}TPP (**9**) and Co^{II}pc (**10**), were also added in two molar equivalents to alkaline reactions of **1**. These compounds lack the sulfonic groups of the previous organometallics; **9** and **10** may be less reactive

due to their poorer water solubility. As can be seen in Fig. 2, **10** converted very little of **1** into cyclized products; any increase in cyclized products as compared to glucose alone was insignificant. However, **9** did provide good yields of cyclized products. This fact supports the earlier speculation that **7** and **8** formed secondary products from primary cyclized products. Thus, the organometallics appear capable of transferring electrons to QMs.

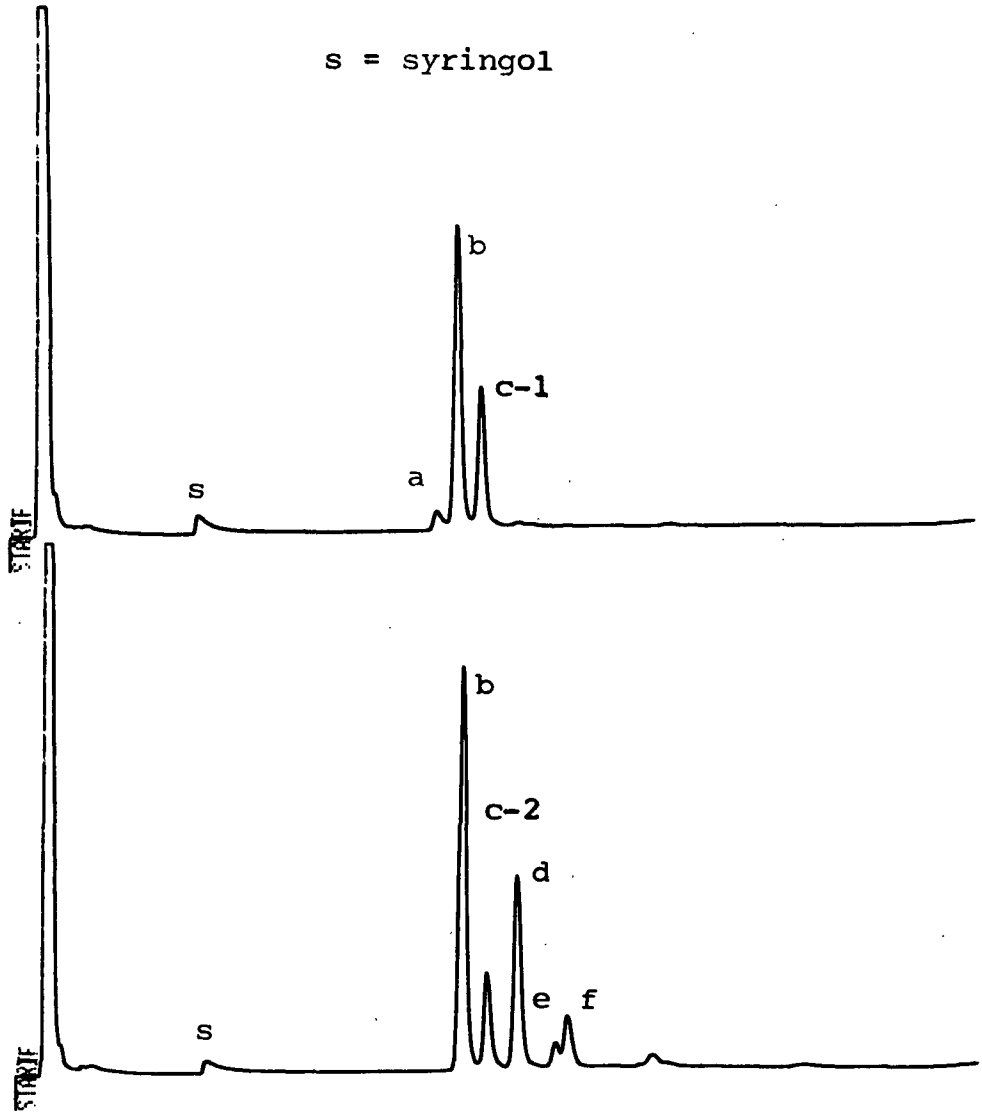
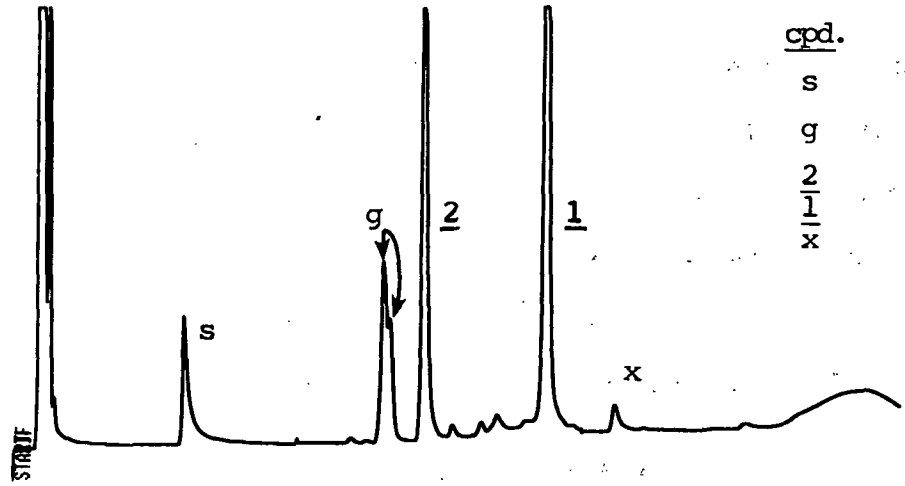
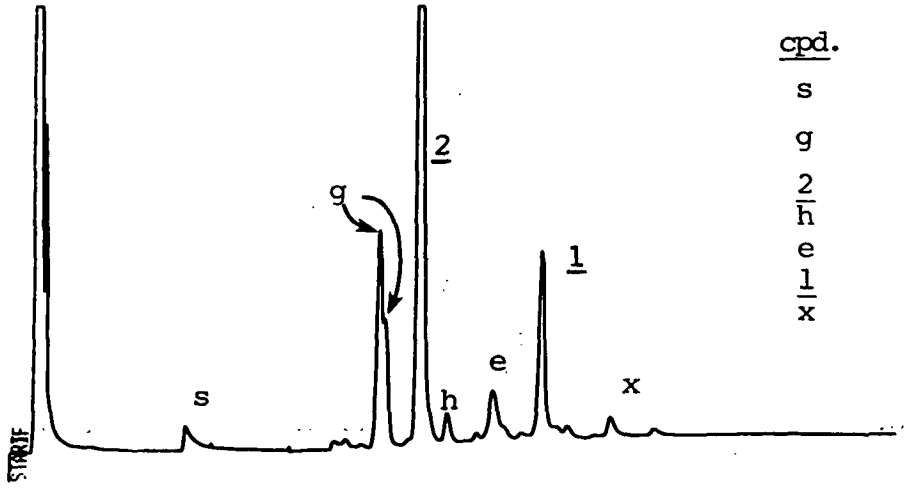


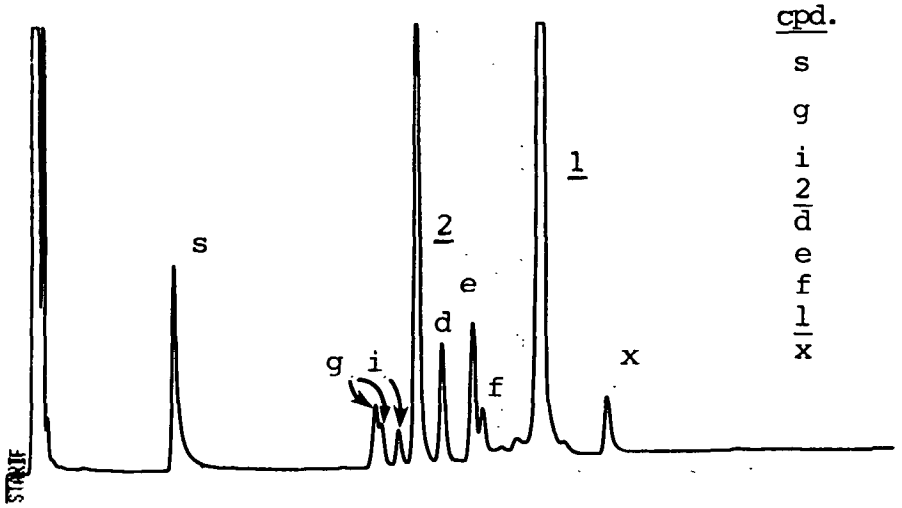
Figure 1. The GC chromatograms of the products formed when **7** (top) and **8** (bottom) were present during an alkaline reaction of **1**. s = syringol, a = unidentified product of MW = 248; b, d, and f = unidentified products of MW = 262, e = tricyclo [7.3.0.$0^{2,7}$] dodecatriene of MW = 262; c-1 and c-2 appear to be a mixture of an unidentified product and **2**. (See the Experimental Section for the mass spectra of the products.)



cpd.	area%
s	9.31
g	9.61
2	6.64
1	27.12
x	44.87
	2.45



cpd.	area%
s	3.40
g	12.09
2	6.44
h	58.24
e	1.61
1	5.42
x	10.82
	1.97



cpd.	area%
s	8.60
g	2.21
i	1.47
2	1.19
d	17.84
e	4.40
f	4.81
1	2.19
x	54.63
	2.65

Figure 2. A comparison of the yield of cyclized products between glucose alone (top) and when **9** (middle) and **10** (bottom) were also added to alkaline reactions of **1**. s = syringol; g = tricyclo [7.3.0.$0^{2,7}$] 2,4,6-dodecatrienes of MW = 232; h = unidentified product of MW = 264; e = tricyclo [7.3.0.$0^{2,7}$] 2,4,6-dodecatriene of MW = 262; d, f, and i = unidentified products of MW = 262; and x = unidentified product of MW = 280. (See the Experimental Section for the mass spectra of the products.)

EXPERIMENTAL

Reaction Procedure

Every reaction solution was prepared in a nitrogen atmosphere with oxygen-free water and 30% ultrapure NaOH. The reactions were conducted in stainless steel pressure vessels (bombs) of 4-mL capacity. Enough water, NaOH, and **1** were added to make a 1N NaOH solution with 0.020 mole/liter of **1**. Except for the organometallics, where the amount of **1** varied due to the small supply of these additives, each bomb was loaded with 0.0196 g of **1** which resulted in a 3.5-mL solution.

The amounts of the additives were as follows: Na_2CO_3 (0.0371 g, 5 molar equivalents), $NaNO_3$ (0.0441 g, 5 molar equivalents), $Na_2S_2O_4$ (0.0609 g, 5 molar equivalents), resorcinol (0.0385 g, 5 molar equivalents), ethylene diamine (0.02 g, 5 molar equivalents), and DMSO (0.03 g, 5 molar equivalents). For the organometallics, each was added in 2 molar equivalents along with 2.1 molar equivalents of glucose.

Bombs containing organometallics were tumbled initially in a 70°C oil bath for 6 hours, which was done to allow for the reduction of the organometallics by the glucose and the degradation of as much of the unoxidized glucose as possible before QMs would be formed. The oil was then heated to 135°C, the temperature at which the bombs containing the other additives were placed in the bath. After the desired length of time at 135°C (4-18 hours), the bombs were cooled in water. The contents of the bombs were neutralized with 2M H_2SO_4 and extracted with chloroform. Analysis of the chloroform solutions was by GC/MS.

Mass Spectra. m/e (%)

3. 214 (23.1, M+), 167 (100.0).

4. 278 (3.7, M+), 224 (8.0), 181 (100.0).

5. 310 (3.8, M+), 213 (100.0).

Compound a. 248 (100.0), 233 (26.1), 205 (54.0), 187 (69.0), 173 (39.4), 153 (32.0).

Compound b. 262 (100.0), 247 (20.9), 219 (18.6), 187 (57.4), 167 (22.9), 159 (17.9).

Compound c-1. 264 (19.0), 262 (67.2), 247 (100.0), 215 (21.1), 168 (28.3), 167 (15.3).

Compound c-2. 264 (52.2), 262 (23.0), 247 (46.2), 215 (9.8), 168 (100.0), 167 (46.2).

Compound d. 262 (100.0), 247 (19.5), 175 (28.9), 167 (21.8).

Compound f. 262 (12.4), 208 (39.6), 206 (21.5), 180 (100.0), 175 (22.2), 167 (87.4).

Compound h. 264 (12.0), 168 (30.9), 167 (100.0).

Compound i. 262 (100), 219 (22.4), 189 (15.3), 187 (72.2), 167 (17.2), 159 (26.4), 154 (19.5).

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APPENDIX II

SYRINGYL ALCOHOL REACTION DATA

The following are tabulated data for the concentrations of syringyl alcohol and its products when syringyl alcohol, in conjunction with various additives, was reacted in 1N NaOH at 135°C for four hours.

1 = syringyl alcohol

2 = disyringylmethane

3 = syringaldehyde

4 = 4-methylsyringol

5 = syringol

Control Reaction (no additives)

Reaction Time, minutes	Concentration (mmoles/liter)				
	1	2	3	4	5
2.5	14.15	0.000	0.273	0.000	0.019
5	14.66	0.023	0.350	0.000	0.045
7.5	14.57	0.340	0.408	0.026	0.073
10	14.49	0.620	0.448	0.057	0.099
15	13.37	1.059	0.510	0.105	0.152
20	12.79	1.410	0.563	0.148	0.197
30	11.06	2.162	0.674	0.242	0.285
40	11.33	2.753	0.793	0.325	0.351
55	8.32	3.572	0.963	0.434	0.454
70	7.24	4.099	1.119	0.520	0.517
85	6.10	4.726	1.220	0.594	0.581
100	6.18	4.913	1.289	0.659	0.629
120	4.97	5.298	1.397	0.727	0.668
140	4.25	5.600	1.470	0.785	0.708
160	4.06	5.635	1.480	0.789	0.714
180	4.01	5.654	1.736	0.824	0.759
210	3.35	5.834	1.830	0.839	0.815
240	2.74	6.022	1.884	0.859	0.815

Control Reaction
(no additives, second experiment)

For 1-5, see p. 93

Reaction Time, minutes	Concentration (mmoles/liter)				
	1	2	3	4	5
2.5	15.57	0.305	0.007	0.000	0.007
5	15.34	0.527	0.001	0.000	0.025
7.5	13.62	0.776	0.041	0.000	0.072
10	15.06	1.022	0.033	0.000	0.088
15	13.03	1.466	0.133	0.025	0.119
20	12.03	1.779	0.225	0.043	0.148
30	10.60	2.370	0.388	0.077	0.200
40	10.17	2.939	0.454	0.074	0.262
55	8.98	--	0.569	0.096	0.280
70	6.76	3.895	0.611	0.103	0.308
85	5.69	4.394	0.721	0.089	0.349
100	5.08	4.515	0.748	0.116	0.376
120	4.95	4.807	0.822	0.168	0.333
140	4.32	4.992	0.825	0.167	0.351
160	2.89	5.206	0.867	0.205	0.420
180	2.21	5.384	0.865	0.183	0.383
210	2.08	5.779	0.862	0.161	0.475
240	1.32	5.822	0.872	0.216	0.472

Control Reaction
(no additives, third experiment)

For 1-5, see p. 93

Reaction Time, minutes	Concentration (mmoles/liter)				
	1	2	3	4	5
5	20.43	0.399	0.170	0.000	0.013
7.5	19.43	0.545	0.140	0.000	0.027
10	16.59	0.695	0.140	0.000	0.044
15	17.63	1.066	0.156	0.023	0.064
20	15.13	1.376	0.224	0.055	0.089
30	13.47	1.918	0.355	0.097	0.128
40	10.83	2.394	0.442	0.113	0.153
55	10.40	2.909	0.558	0.148	0.190
70	7.55	3.359	0.669	0.171	0.249
85	6.78	3.726	0.736	0.166	0.243
100	5.12	3.958	0.773	0.211	0.263
120	6.53	3.982	0.930	0.235	0.282
140	5.36	4.625	0.904	0.219	0.290
160	4.42	4.992	0.976	0.261	0.292
180	4.04	5.188	0.985	0.299	0.325
210	3.65	5.421	1.072	0.307	0.315
240	0.51	5.704	1.149	0.354	0.315

Trimethylphenol

For 1-5, see p. 93

Reaction Time, minutes	Concentration (mmoles/liter)				
	1	2	3	4	5
2.5	17.34	0.289	0.270	0.025	0.023
5	16.48	0.473	0.296	0.027	0.064
7.5	16.11	0.705	0.298	0.053	0.092
10	15.84	0.945	0.331	0.071	0.127
15	14.47	1.379	0.410	0.100	0.199
20	13.60	1.781	0.456	0.128	0.253
30	11.84	2.472	0.560	0.189	0.363
40	10.65	3.058	0.646	0.244	0.452
55	8.86	3.700	0.758	0.305	0.546
70	7.31	4.245	0.870	0.354	0.629
85	6.43	4.689	0.845	0.404	0.685
100	5.70	5.086	0.903	0.438	0.740
120	4.57	5.531	0.940	0.480	0.786
140	4.01	5.816	0.993	0.509	0.830
160	3.30	5.998	1.031	0.541	0.863
180	2.90	6.310	1.053	0.565	0.893
210	2.28	6.532	1.080	0.590	0.914
240	1.68	6.639	1.099	0.622	0.945

Dinitrobenzoic Acid

For 1-5, see p. 93

Reaction Time, minutes	Concentration (mmoles/liter)				
	1	2	3	4	5
2.5	14.93	0.289	0.844	0.000	0.022
5	18.43	0.328	1.087	0.000	0.025
7.5	13.21	0.481	1.377	0.006	0.034
10	12.41	0.627	1.792	0.000	0.044
15	11.42	0.909	2.058	0.000	0.060
20	12.42	1.174	2.097	0.019	0.083
30	10.52	1.566	2.485	0.026	0.112
40	11.14	1.969	2.852	0.033	0.139
55	8.60	2.320	3.184	0.048	0.167
70	8.34	2.713	3.476	0.054	0.190
85	7.08	3.000	3.704	0.056	0.207
100	5.99	3.073	3.698	0.064	0.224
120	5.91	3.334	3.784	0.061	0.244
140	6.82	3.612	3.996	0.075	0.255
160	5.82	3.753	3.982	0.075	0.264
180	5.72	3.954	4.127	0.074	0.271
210	5.61	4.049	4.047	0.082	0.281
240	4.92	4.069	4.196	0.081	0.288

Dinitrobenzoic Acid
(Repeat analysis)

For 1-5, see p. 93

Reaction Time, minutes	Concentration (mmoles/liter)				
	1	2	3	4	5
5	20.74	0.693	1.055	0.018	0.024
10	13.83	0.695	1.856	0.023	0.044
20	12.78	1.180	2.109	0.043	0.077
40	9.11	1.972	2.842	0.061	0.134
70	5.33	2.693	3.469	0.080	0.188
100	2.45	3.054	3.653	0.090	0.222
140	1.97	3.596	3.853	0.100	0.252
180	0.91	3.905	3.919	0.098	0.270
240	0.00	4.033	4.002	0.103	0.290

Dinitrobenzoic Acid
(Second experiment)

For 1-5, see p. 93

Reaction Time, minutes	Concentration (mmoles/liter)				
	1	2	3	4	5
2.5	14.82	0.254	0.659	0.059	0.002
5	13.64	0.430	0.907	0.073	0.018
7.5	13.76	0.598	1.166	0.049	0.031
10	11.65	0.795	1.384	0.068	0.048
15	9.99	1.148	1.541	0.067	0.071
20	8.69	1.455	1.861	0.083	0.095
30	7.38	1.981	2.062	0.091	0.130
40	6.22	2.366	2.148	0.086	0.146
55	4.74	3.153	2.299	0.106	0.189
70	3.87	3.798	2.274	0.109	0.206
85	3.47	3.944	2.133	0.118	0.232
100	2.04	4.198	2.723	0.109	0.254
120	1.53	4.410	2.812	0.115	0.276
140	0.48	4.487	3.007	0.098	0.291
160	1.39	4.710	3.008	0.098	0.292
180	0.34	4.871	3.029	0.110	0.326
210	0.29	4.902	3.103	0.102	0.311
240	0.00	5.165	3.329	0.098	0.303

Dinitrobenzoic Acid
(Repeat analysis of the second experiment)

For 1-5, see p. 93

Reaction Time, minutes	Concentration (mmoles/liter)				
	1	2	3	4	5
2.5	17.51	0.215	0.748	0.000	0.000
5	15.51	0.417	0.992	0.000	0.023
7.5	14.60	0.618	1.237	0.000	0.042
10	14.00	0.837	1.405	0.000	0.049
15	12.49	1.182	1.595	0.000	0.087
20	11.29	1.511	1.752	0.000	0.098
30	9.20	2.021	1.957	0.000	0.140
40	7.71	2.382	2.109	0.000	0.173
55	6.36	2.850	2.270	0.000	0.216
70	4.72	3.172	2.135	0.000	0.250
85	3.82	3.396	2.323	0.000	0.257
100	2.76	3.630	2.662	0.000	0.268
120	2.16	3.809	2.802	0.000	0.285
140	0.80	4.096	2.824	0.000	0.315
160	1.11	4.060	2.902	0.011	0.333
180	0.23	4.207	2.995	0.000	0.335
210	0.00	4.367	3.117	0.004	0.338
240	0.00	4.500	3.145	0.000	0.354

Sodium Persulfate

For 1-5, see p. 93

Reaction Time, minutes	Concentration (mmoles/liter)				
	1	2	3	4	5
2.5	11.24	0.070	2.482	0.052	0.056
5	10.85	0.035	2.474	0.048	0.081
7.5	10.55	0.157	2.470	0.054	0.108
10	9.83	0.228	2.477	0.073	0.123
15	9.21	0.426	2.458	0.095	0.167
20	8.44	0.616	2.488	0.111	0.203
30	7.41	0.943	2.455	0.148	0.271
40	6.61	1.276	2.506	0.183	0.339
55	5.68	1.629	2.516	0.219	0.410
70	4.71	1.959	2.553	0.252	0.470
85	3.18	2.221	2.538	0.277	0.518
100	3.18	2.373	2.456	0.296	0.558
120	2.48	2.606	2.480	0.320	0.608
140	2.30	2.847	2.486	0.330	0.648
160	1.33	3.055	2.438	0.350	0.680
180	0.89	3.223	2.418	0.367	0.712
210	0.32	3.410	2.419	0.378	0.757
240	0.00	3.624	2.462	0.359	0.798

Potassium Ferricyanide

For 1-5, see p. 93

Reaction Time, minutes	Concentration (mmoles/liter)				
	1	2	3	4	5
2.5	5.02	0.213	1.893	0.000	0.023
5	7.07	0.003	1.909	0.000	0.024
7.5	9.52	0.002	1.907	0.000	0.027
10	7.90	0.000	1.942	0.000	0.034
15	1.89	0.000	1.875	0.000	0.031
20	3.30	0.000	1.901	0.008	0.038
30	3.05	0.000	1.892	0.063	0.043
40	1.00	0.000	1.853	0.103	0.050
55	0.22	0.000	1.760	0.177	0.060
70	1.96	0.024	1.849	0.263	0.068
85	1.39	0.029	1.865	0.333	0.073
100	0.00	0.049	1.747	0.395	0.083
120	2.04	0.056	1.742	0.470	0.088
140	0.90	0.053	1.650	0.551	0.091
160	1.35	0.074	1.657	0.655	0.098
180	0.00	0.087	1.649	0.743	0.104
210	0.00	0.106	1.624	0.823	0.111
240	3.83	0.136	1.650	1.005	0.114

2 Equivalents Anthrahydroquinone

For 1-5, see p. 93

Reaction Time, minutes	Concentration (mmoles/liter)				
	1	2	3	4	5
2.5	7.34	0.134	0.981	0.397	0.042
5	6.11	0.022	0.727	0.570	0.049
7.5	4.49	0.027	0.763	0.765	0.065
10	3.66	0.035	0.780	0.858	0.075
15	2.68	0.059	0.885	1.151	0.098
20	2.07	0.084	0.979	1.324	0.114
30	1.66	0.116	1.158	1.607	0.144
40	1.16	0.146	1.275	1.787	0.169
55	1.11	0.181	1.421	1.962	0.203
70	0.87	0.209	1.568	2.084	0.229
85	0.94	0.218	1.690	2.245	0.257
100	0.29	0.245	1.804	2.214	0.285
120	0.53	0.236	1.706	2.246	0.310
140	0.79	0.284	1.942	2.347	0.355
160	0.28	0.299	1.920	2.449	0.394
180	0.30	0.263	1.845	2.383	0.420
210	0.20	0.271	1.927	2.345	0.453
240	0.07	0.284	2.030	2.383	0.505

2 Equivalents Anthrahydroquinone
(Second experiment)

For 1-5, see p. 93

Reaction Time, minutes	Concentration (mmoles/liter)				
	1	2	3	4	5
2.5	4.61	0.062	0.000	0.170	0.001
5	3.77	0.047	0.088	0.305	0.004
7.5	3.76	0.138	0.355	0.747	0.034
10	4.89	0.188	0.547	0.946	0.045
15	6.76	0.219	0.672	1.142	0.067
20	3.69	0.219	0.637	1.265	0.080
30	3.92	0.278	0.856	1.475	0.089
40	2.39	0.316	0.910	1.663	0.128
55	2.79	0.341	1.103	1.708	0.160
70	2.19	0.360	1.088	1.786	0.168
85	2.63	0.393	1.506	1.785	0.182
100	1.59	0.366	1.181	1.659	0.197
120	1.95	0.408	1.339	1.676	0.222
140	1.43	0.509	1.739	1.737	0.254
160	2.93	0.474	2.167	1.836	0.258
180	2.54	0.474	2.107	1.772	0.287
210	4.34	0.502	2.427	1.895	0.311
240	3.26	0.501	2.298	1.869	0.344

2 Equivalents Anthrahydroquinone
(Repeat analysis of the second experiment)

For 1-5, see p. 93

Reaction Time, minutes	Concentration (mmoles/liter)				
	1	2	3	4	5
2.5	4.56	0.063	0.000	0.005	0.014
5	4.02	0.059	0.092	0.128	0.026
7.5	4.14	0.123	0.221	0.520	0.046
10	4.66	0.135	0.479	0.683	0.054
15	4.25	0.178	0.617	0.974	0.068
20	2.87	0.214	0.647	1.197	0.091
30	2.90	0.255	0.837	1.493	0.111
40	1.98	0.290	0.935	1.585	0.125
55	2.12	0.349	1.077	1.821	0.155
70	2.00	0.353	1.100	1.891	0.165
85	1.99	0.376	1.399	1.922	0.185
100	0.99	0.398	1.326	1.730	0.196
120	1.31	0.413	1.414	1.686	0.218
140	0.90	0.450	1.728	1.810	0.244
160	1.76	0.487	1.997	1.855	0.259
180	1.53	0.500	2.110	1.903	0.273
210	2.08	0.518	2.367	1.982	0.314
240	1.66	0.529	2.305	1.930	0.321

0.5 Equivalent Anthrahydroquinone

For 1-5, see p. 93

Reaction Time, minutes	Concentration (mmoles/liter)				
	1	2	3	4	5
2.5	25.18	0.159	0.482	0.046	0.018
5	22.40	0.393	0.873	0.179	0.056
7.5	23.11	0.563	0.998	0.286	0.088
10	27.08	0.737	1.245	0.406	0.122
15	16.49	1.100	1.828	0.601	0.180
20	14.92	1.297	2.179	0.758	0.234
30	12.03	1.720	3.013	1.052	0.316
40	7.50	1.968	3.649	1.292	0.382
55	5.90	2.280	4.397	1.597	0.467
70	3.75	2.392	4.968	1.801	0.524
85	2.02	2.536	5.349	1.961	0.569
120	0.62	2.630	6.157	2.211	0.637
140	0.72	2.702	6.567	2.282	0.671
160	0.02	2.802	6.739	2.332	0.700
180	0.00	2.766	6.540	2.420	0.725
210	0.00	2.816	6.889	2.447	0.753
240	0.00	2.883	7.174	2.489	0.782

0.1 Equivalent Anthrahydroquinone

For 1-5, see p. 93

Reaction Time, minutes	Concentration (mmoles/liter)				
	1	2	3	4	5
2.5	17.72	0.282	0.441	0.059	0.027
5	17.20	0.425	0.522	0.056	0.048
7.5	16.37	0.722	0.672	0.104	0.083
10	15.78	0.887	0.766	0.121	0.101
15	14.47	1.300	0.978	0.194	0.157
20	13.72	1.679	1.131	0.269	0.203
30	12.15	2.288	1.483	0.414	0.284
40	10.73	2.757	1.625	0.553	0.352
55	8.97	3.352	1.944	0.732	0.434
70	7.46	3.641	2.221	0.886	0.495
85	6.41	4.020	2.443	1.000	0.542
100	5.38	4.317	2.508	1.101	0.583
120	4.50	4.448	2.754	1.218	0.622
140	3.65	4.688	2.929	1.320	0.655
160	3.12	4.983	2.942	1.398	0.680
180	2.66	5.309	3.198	1.568	0.740
210	2.00	5.047	3.161	1.557	0.726
240	1.44	5.288	3.170	1.621	0.739

2 Equivalents Glucose

For 1-5, see p. 93

Reaction Time, minutes	Concentration (mmoles/liter)				
	1	2	3	4	5
2.5	14.92	0.216	0.003	0.117	0.013
5	14.25	0.238	0.013	0.227	0.020
7.5	12.84	0.311	0.015	0.328	0.033
10	11.50	0.368	0.000	0.408	0.039
15	10.12	0.541	0.000	0.574	0.051
20	9.33	0.678	0.000	0.712	0.065
30	7.59	0.968	0.000	0.922	0.091
40	6.46	1.194	0.000	1.047	0.111
55	5.41	1.436	0.027	1.168	0.136
70	4.68	1.621	0.052	1.271	0.164
85	3.92	1.807	0.056	1.316	0.179
100	3.55	1.940	0.074	1.369	0.195
120	3.33	2.090	0.146	1.457	0.242
140	2.95	2.290	0.209	1.490	0.246
160	2.44	2.343	0.252	1.500	0.256
180	2.14	2.416	0.228	1.546	0.272
210	1.87	2.550	0.304	1.549	0.286
240	1.52	2.652	0.317	1.570	0.293

2 Equivalents Glucose
(Second experiment)

For 1-5, see p. 93

Reaction Time, minutes	Concentration (mmoles/liter)				
	1	2	3	4	5
5	14.22	0.466	0.044	0.157	0.017
10	11.79	0.392	0.000	0.348	0.032
20	8.93	0.709	0.000	0.632	0.064
40	6.15	1.314	0.027	0.942	0.125
70	3.92	1.823	0.030	1.070	0.175
100	2.62	2.221	0.090	1.179	0.217
140	1.32	2.584	0.123	1.266	0.254
180	0.46	2.783	0.181	1.338	0.282
240	0.00	3.062	0.212	1.425	0.311

2 Equivalents Glucose
(Third experiment)

For 1-5, see p. 93

Reaction Time, minutes	Concentration (mmoles/liter)				
	1	2	3	4	5
2.5	12.41	0.102	0.000	0.153	0.010
5	10.31	0.193	0.000	0.284	0.021
7.5	9.33	0.228	0.045	0.351	0.026
10	8.73	0.258	0.000	0.417	0.033
15	6.32	0.459	0.000	0.680	0.051
20	5.43	0.559	0.000	0.819	0.077
30	4.32	0.673	0.000	1.013	0.092
40	3.29	0.753	0.000	1.107	0.112
55	2.51	0.846	0.000	1.236	0.133
70	1.84	0.906	0.000	1.303	0.149
100	1.31	1.005	0.000	1.427	0.173
120	1.14	1.045	0.000	1.483	0.183
140	0.84	1.071	0.000	1.518	0.186
160	0.65	1.095	0.000	1.553	0.201
180	0.94	1.137	0.022	1.569	0.201
210	0.57	1.144	0.070	1.606	0.212
240	0.47	1.167	0.069	1.612	0.221

5 Equivalents Glucose

For 1-5, see p. 93

Reaction Time, minutes	Concentration (mmoles/liter)				
	1	2	3	4	5
2.5	8.12	0.183	0.299	0.122	0.035
5	5.03	0.142	0.130	0.247	0.034
7.5	3.00	0.198	0.153	0.392	0.049
10	1.68	0.181	0.129	0.415	0.052
15	0.00	0.165	0.132	0.509	0.058
20	0.00	0.207	0.156	0.571	0.074
30	0.00	0.220	0.123	0.728	0.074
40	0.00	0.222	0.099	0.785	0.081
55	0.00	0.225	0.103	0.857	0.089
70	0.00	0.215	0.079	0.852	0.092
85	0.00	0.204	0.075	0.914	0.098
100	0.00	0.177	0.072	0.772	0.085
120	0.00	0.274	0.116	0.975	0.118
140	0.00	0.261	0.091	0.978	0.114
160	0.00	0.264	0.098	1.017	0.131
180	0.00	0.266	0.106	1.024	0.123
210	0.00	0.262	0.111	1.061	0.139
240	0.00	0.271	0.126	1.051	0.139

2 Equivalents Sodium Sulfide

For 1-5, see p. 93

Reaction Time, minutes	Concentration (mmoles/liter)				
	1	2	3	4	5
2.5	13.32	0.092	0.000	0.020	0.007
5	10.25	0.067	0.000	0.042	0.014
7.5	9.18	0.095	0.000	0.000	0.022
10	8.08	0.162	0.000	0.000	0.026
15	7.05	0.298	0.000	0.001	0.036
20	6.72	0.408	0.000	0.012	0.045
30	6.62	0.631	0.000	0.014	0.061
40	6.22	0.858	0.000	0.026	0.077
55	5.97	1.165	0.000	0.033	0.101
70	5.75	1.468	0.000	0.049	0.122
85	5.38	1.712	0.000	0.060	0.142
100	5.26	1.978	0.000	0.072	0.161
120	5.00	2.270	0.066	0.086	0.182
140	4.64	2.555	0.124	0.100	0.202
160	4.52	2.805	0.181	0.120	0.215
180	4.28	3.077	0.192	0.113	0.237
210	4.08	3.392	0.295	0.143	0.254
240	3.85	3.673	0.386	0.165	0.272

2 Equivalents Sodium Sulfide
(Second experiment)

For 1-5, see p. 93

Reaction Time, minutes	Concentration (mmoles/liter)				
	1	2	3	4	5
2.5	15.85	0.169	0.000	0.110	0.018
5	14.03	0.232	0.000	0.117	0.032
7.5	14.32	0.336	0.000	0.182	0.044
10	9.48	0.432	0.000	0.059	0.050
15	8.64	0.637	0.000	0.064	0.072
20	8.06	0.833	0.000	0.051	0.089
30	8.93	1.220	0.000	0.041	0.122
40	7.64	1.566	0.000	0.056	0.152
55	6.65	2.025	0.001	0.054	0.197
70	6.45	2.409	0.175	0.101	0.226
85	6.24	2.772	0.245	0.094	0.247
100	6.14	3.067	0.262	0.097	0.268
120	5.81	3.453	0.339	0.124	0.299
140	5.68	3.816	0.354	0.110	0.314
160	5.41	4.116	0.407	0.105	0.348
180	4.98	4.387	0.510	0.167	0.349
210	4.75	4.729	0.561	0.185	0.369
240	5.39	5.038	0.554	0.175	0.405

1 Equivalent Sodium Sulfide and Anthrahydroquinone

For 1-5, see p. 93

Reaction Time, minutes	Concentration (mmoles/liter)				
	1	2	3	4	5
2.5	18.64	0.503	0.036	0.130	0.019
5	16.56	0.133	0.118	0.202	0.031
7.5	14.00	0.072	0.223	0.265	0.032
10	12.34	0.092	0.294	0.346	0.038
15	10.50	0.144	0.404	0.449	0.049
20	7.86	0.192	0.520	0.511	0.059
30	6.38	0.281	0.757	0.664	0.079
40	4.87	0.386	0.983	0.771	0.094
55	5.61	0.483	1.274	0.915	0.115
70	3.52	0.570	1.544	0.993	0.134
85	3.42	0.618	1.738	1.082	0.150
100	3.37	0.650	1.861	1.131	0.162
120	2.88	0.701	2.069	1.194	0.177
140	2.52	0.735	2.212	1.247	0.190
160	1.87	0.770	2.387	1.309	0.202
180	1.64	0.770	2.515	1.322	0.210
210	1.80	0.820	2.701	1.382	0.226
240	1.83	0.846	2.756	1.421	0.239

2 Equivalents Sodium Sulfide and Glucose

For 1-5, see p. 93

Reaction Time, minutes	Concentration (mmoles/liter)				
	1	2	3	4	5
4.5	7.01	0.148	0.012	0.452	0.027
8	5.02	0.193	0.000	0.684	0.041
10	4.35	0.244	0.000	0.803	0.046
15	3.31	0.341	0.000	1.044	0.063
20	2.88	0.430	0.000	1.180	0.070
30	2.32	0.574	0.000	1.444	0.089
40	1.92	0.709	0.009	1.673	0.106
55	1.28	0.810	0.000	1.812	0.125
70	0.94	0.918	0.026	1.925	0.140
85	0.71	1.000	0.061	2.031	0.151
100	0.52	1.077	0.046	2.121	0.160
120	0.33	1.150	0.089	2.241	0.173
140	0.13	1.173	0.113	2.279	0.191
160	0.02	1.216	0.160	2.351	0.204
180	0.00	1.228	0.178	2.401	0.219
210	0.00	1.255	0.235	2.483	0.232
240	0.00	1.266	0.287	2.541	0.242